Bridge Measurements of the Dielectric Relaxation Spectrum of Ice with Blocking Electrodes

by

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Abstract

This paper described measurements of the dielectric constant and of the conductivity on pure ice. Using three-terminal bridge covered a wide range of temperature and frequency with (a) blocking layers inserted between the samples and electrodes and (b) stainless steel guard electrodes. The mathematical model representing the dielectric properties of ice is derived from an electric equivalent circuit model with includes the parallel plate capacitor by which electrical potentials are applied to a block of ice. The purpose of this report is to discuss methods of analyzing dielectric dispersion parameters and questions of interpretation of such measurements. We concern with the frequency and temperature dependence of dielectric behavior in alternating fields. The relaxation effects arising from failure of the polarization to each equilibrium with the applied field are conveniently described by the complex dielectric constant.

Acknowledgement

I would like to express my gratitude to the many people who assisted and encouraged me during the course of my studies.

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Most importantly, I would like to express my deepest appreciation to Dr. Gerardo W. Gross, my advisor, for his constant encouragement, patient guidance, valuable advice and continued financial support throughout this study.

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Section 1 : Introduction

This study deals with the dielectric relaxation spectrum of ice, comparing the dielectric data measured by bridge method with a different kinds of electrode over a wide range of frequency and temperature. Then, in accurate determine the parameters of the mathematical model.

The most generally used methods for measuring dielectric constant ϵ' and dielectric loss ϵ'' is compose of the measurement of the capacitance C_0 of an empty condenser and the capacitance C, the resistance R of the condenser filled with the dielectric material (ICE). The measurement involves to determine the impedance (voltage/current) of the circuit element use a cell containing the dielectric. This impedance is

$$Z = \frac{1}{i\omega C + 1/R} = \frac{1}{i\omega C_0 \epsilon^*}, \tag{1.1}$$

$$\epsilon^* = \epsilon' - i\epsilon''. \tag{1.2}$$

Substitute Eq. (1.2) in Eq. (1.1), separate the real and imaginary parts we can obtained $\epsilon' = \frac{C}{C_0}$, and $\epsilon'' = \frac{1}{\omega R C_0}$.

Bridge method is principal useful method for the the measurement of dielectric loss and of the dielectric constant of dielectric materials. The general theory of the bridge methods is reducing to zero the voltage between two opposite corners, a condition which occurs when the ratio of the impedance of two adjacent bridge arms. The capacitance bridges commonly used for the measurement of dielectric constant and loss contain two resistance arms, the so-called ratio arms, and two capacitance arms. In such bridges inductance is kept to a minimum and, by symmetrical construction of the bridge parts, is made to cancel out. Since, however, the material to be measured has an effective conductance if it possesses any loss, and since small inequalities in resistance may occur elsewhere in the system, small, noninductively wound resistances are placed in series with the capacitances or large, noninductively wound resistance in parallel with them. If R_1 is the resistance in parallel with the precision measuring condenser and the measuring cell of resistance R_m, and R_2 is the resistance in parallel with the other capacitance arm of the bridge, then, at balance, $\frac{1}{R_m} = \frac{1}{R_2} - \frac{1}{R_1}$. The specific conductance K of dielectric under measurement in the cell is then

$$K = \frac{0.0885}{C_0 R_m},$$

where C_0 is the geometrical capacitance (in pF) of the empty cell. The loss factor of the material under measurement can be calculated as:

$$\epsilon'' = \frac{1.8\times10^{12}}{f} k,$$

where f is the frequency.

The capacitance can be measured forms an entire arm of the bridge. The absolute accuracy of such an instrument can often be greatly improved by substituting a precision measuring condenser in this arm of the bridge, balancing the bridge, attaching the cell to be measured in parallel with the precision condenser, and turning down the latter until the bridge is balanced again. The difference between the two condenser readings usually gives the unknown capacitance with an accuracy unobtainable with an instrument in another arm of the bridge [1].

In this study we designed a cell containing a stainless-steel guard electrodes and blocking layers [2]. The first achieves automatic adjustment of the potential of the guard electrode and serves as an electrostatic shield of the collector, thus decrease the direct current (d.c.) conductivity of ice [3]. The second achieves inserting thin layers of a loss-free dielectric (Teflon foil) between the metal contacts and specimen, thus depresses the electrode space-charge effects, more detail technique and theory in [4, 5].

Section 2 : Dielectrical properties of ICE

From X-ray studies just know the location of the oxygen atoms [6]. The possible structure, identified by neutron diffraction, is D_{6h}^{4}—$P6_3/mmc$. Each oxygen atom is at the center of a tetrahedraction where the four neighboring atoms are the vertices at a distance of 2.76A (=R). The c/a ratio is almost the same as the regular tetrahedron. In the plane perpendicular to the C-axis, there is a network of regular hexagons, each having three atoms above and three below the median plane (Fig. 2.1). The hexagons in different planes are superimposed so as to leave channels passing right through the lattice. The planes parallel to the c-axis consist of irregular hexagons with 2 atoms in front of and four behind the median plane (Fig. 2.2) [7].

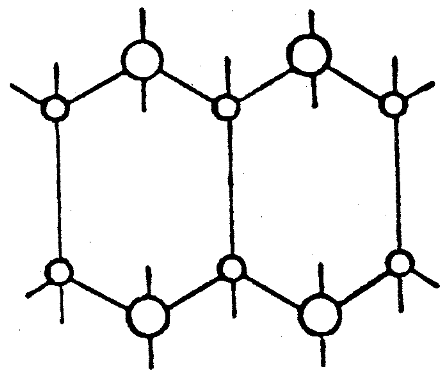


Fig. 2.1 Plane perpendicular to the C-axis.

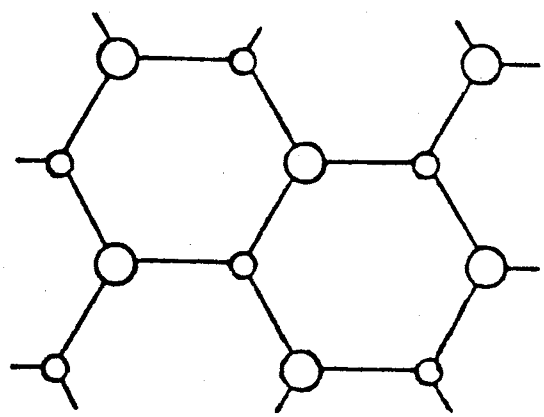


Fig. 2.2 Plane parallel to the C-axis.

The similarity between the infra-red and Raman spectra of ice and water vapor led Bernal and Fowler [8] to make the three following hypotheses, which take account of the fact that the identity of the water molecule is conserved in the crystal:

1. The hydrogen atoms are on the lines joining neighboring oxygen atoms.
2. On each bond, there is one hydrogen atom.
3. Each oxygen atom has two hydrogen atoms as nearest neighbors at a distance of 0.99A.

The relationship between different configurations and their thermodynamic properties has been discussed by Granicher [9]. He showed that the energy differences were very small and played no part near the freezing point, thus confirming the neutron diffraction studies made by Wollan, Davidson and Shull [10] on polycrystalline D_2O ice and on single-crystals of D_2O ice: on a macroscopic scale one finds on average, on each bond, one half of a hydrogen atom near each oxygen atom. So that we can define as a perfect crystal one which has no electrical conductivity if this is not produced by the deformation of molecules.

In the Ice crystal structure have two sorts of elementary defects, which violate the Bernal-Fowler rules:

a. There exist H_3O^+ and OH^- ions in which an atom of oxygen is surrounded by three and one hydrogen atoms respectively.
b. There exist vacant (L) O-O bonds and OH-OH bonds occupied twice (D).

The existence of ions is deduced by analogy with the case of water. The existence of orientation or valency defects was postulated by Bjerrum [11]. We will consider the two kinds of defects, which are the only ones which can explain the electrical behavior. In this study, we will not put forward any hypotheses on the way in which they are produced but we will impose the following conditions:

1. During the passage of a current, the distribution and orientation of the defects is statistical.

2. At constant temperature, their orientation is in thermodynamic equilibrium. The recombination of H_3O^+ with OH^-, L with D is compensated by dissociation. To approximate the first, the equilibrium is not influenced by variation in concentration.

3. There is no recombination or association between ions and defects.

4. The concentration of defects is much less than that of normal bonds and molecules, but sufficiently large to assure the validity of statistical calculation.

5. The variation of concentration over distances of the order of the lattice constant is very small.

Generally, in the crystal we have the following assumptions:

a. If other defects are present, (like chemical impurities, dislocations etc.) their diffusion and mobility are zero.

b. Temperature and pressure are constant.

On the other hand, in connection with the Bernal-Fowler hypotheses we assume that each molecule retains its electron cloud and hence, we can say that the electronic conductivity is zero for direct current. On introducing the probabilities of transfer, one can calculate the displacement of the defects taking into account the influence of diffusion and electrical potentials and especially unexpected modification in the lattice. One obtains a formula for the currents which gives directly the electrical conductivity or the diffusion constant.

Pure ice single crystals seem to act as a proton-memory device allowing L- and D- defect motion but restricting ionic transfer of protons to outer and inner crystal boundaries. Its dielectric relaxation spectrum can be broken down into a number of discrete spectra and the current transient into a sequency of contributions [4]. In pure ice, both Bjerrum defects, which are in equal number, are the major carriers and responsible for the high frequency conductivity σ_∞, the relaxation time τ and the static dielectric constant ϵ_s. The ions, also in equal number, are the minor carriers, and responsible for the DC conductivity σ_0.

The electrical properties of ice can be explained by the presence of four mobile structural defects of the lattice which are the ions H_3O^+ and OH^-, and the Bjerrum or valence defects. The opposite action of both sorts on the proton configuration determines the DC conductivity and the predominance of one of them is necessary for the occurrence of the high dielectric constant and its Debye relaxation. The microscopical charge transfers, accompanying the movement of the defects, allow the definition of dynamical defect charges, which in turn relate the electrical parameters with the defect concentrations and determines their tensorial character. The defects respond also to concentration, pressure and temperature gradients, which induce in the crystal differences of the electrical potential. The defect transport occurs by proton jumps on neighboring lattice sites, either with a thermal activation over a potential step or by a tunnel effect through the step.

Section 3 : Theory

Characteristic of dielectric and relaxation theory, based on simple molecular or macroscopic model that we can describe a time rate of change of polarization, or other response, which is proportional to the difference of polarization from its equilibrium value. In general, the complex dielectric constant can expressed by

$$\epsilon^* = \epsilon' - j\epsilon'' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + j\omega\tau_0}, \tag{3.1}$$

for the complex dielectric constant ϵ^* as a function of frequency f ($\omega/2\pi$), where ϵ' and ϵ'' are the real and imaginary parts of ϵ^*, ϵ_0 is the limiting (real) values of very low (zero) frequency (or called static dielectric constant), ϵ_∞ is the limiting (real) values of ϵ^* at high (infinity) frequency, and τ_0 is the dipolar relaxation time [12].

Separate the Eq. (3.1) into the real and the imaginary parts we can get following equations :

$$\epsilon' \equiv \epsilon'(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + (\omega\tau_0)^2}, \tag{3.2a}$$

$$\epsilon'' \equiv \epsilon''(\omega) = \frac{(\epsilon_0 - \epsilon_\infty)\omega\tau_0}{1 + (\omega\tau_0)^2}. \tag{3.2b}$$

In practice, there are two useful procedures to approach these parameters:

Employ the complex plane locus of ϵ' versus ϵ'', which, if Eqs. (3.1) and (3.2) are valid, is the semicircle of the plot of ϵ' vs. ϵ'' with center on the real axis and intercepts on this axis at ϵ_0 and ϵ_∞. This representation, often referred to as the Cole-Cole plot, is useful whether or not the actual data conform to such a semicircle, and if they do the determination of the best semicircle can be quite precisely got. The intercepts of a satisfactory fit give ϵ_0 and ϵ_∞ directly, but the value of τ_0 is not accurately determined from the plot, although it can often be estimated with fair accuracy from the interpolated frequency of the midpoint of the semicircle.

Alternative graphical or analytical methods, which have been found extremely useful and convenient, can be based on the real and imaginary parts of Eq. (3.1) obtained after multiplication by $1+j\omega\tau_0$. These are

$$\epsilon' = \epsilon_0 - \tau_0(\omega\epsilon''), \tag{3.3}$$

$$\epsilon' = \epsilon_\infty + (1/\tau_0)(\epsilon''/\omega). \tag{3.4}$$

The advantage of the equations is that they are linear relations in the measured quantities ϵ', $\omega\epsilon''$, and ϵ''/ω, and from them, if they are satisfied, the parameters ϵ_0, ϵ_∞, τ_0 can be derived as intercepts and slopes without using assumed values.

There are a number of advantages from analysis of simple Debye dispersions. Eq. (3.2) are particularly useful if the directly measured quantities are equivalent parallel capacitance Cp and conductance Gp, as a plot of Cp versus Gp is a straight line of slope $-\tau_0$. This is because Cp and Gp for a dielectric with simple relaxation are proportional to ϵ' and $\omega\epsilon''$, the determination of a time from the measurements without explicit use of frequency or time resulting from the ratio of consistent units of Cp and Gp having dimensions of time. It may be noted also that the same value of τ_0 will be obtained if stray parallel capacitance and conductance are present, provided that these are frequency independent. A second advantage is that systematic errors become evident which may be concealed or obscured in trial and error fitting of Eq. (3.1) to data, and the use of Eqs. (3.2) and (3.3) has on several occasions made implications or errors of experimental measurements apparent.

We can expand this theory, if the Debye dispersion included a dc (ionic) conductivity σ_0, the complex dielectric constant of ice Eq. (3.1) can expressed by

$$\epsilon^*(\omega) = {}' - j\epsilon'' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1+j\omega\tau_0} - j\frac{\sigma_0}{\omega\epsilon_0}, \tag{3.5}$$

where

σ_0 : Zero-frequency limit of the bulk conductivity (dc conductivity).

ϵ_0 : permittivity of free space.

the real component the same as Eq. (3.2a), the imaginary component can expressed by

$$\epsilon'' \equiv \epsilon''(\omega) = \frac{\sigma_0}{\omega\epsilon_0} + \frac{\epsilon_0 - \epsilon_\infty}{1+(\omega\tau_0)^2}\omega\tau_0. \tag{3.6}$$

From above equation, the dc conductivity contributed to the imaginary part (dielectric loss). In the same way, we can use the above methods figure out the parameters for these equations.

If we assume that the dielectric relaxation spectrum of ice is contributed to a small number of single dipolar relaxations [9, 10], so that the above Eqs. (3.2a) and (3.6) became summations*

$$\epsilon' = \epsilon_\infty + \sum_{i=1}^{m} \frac{\epsilon_{0i} - \epsilon_{\infty i}}{1+(1+\omega\tau_{0i})^2}, \tag{3.7}$$

$$\epsilon'' = \frac{\sigma_0}{\omega\epsilon_0} + \sum_{i=1}^{m} \frac{\epsilon_{0i} - \epsilon_{\infty i}}{1+(\omega\tau_{0i})^2}\omega\tau_{0i}, \tag{3.8}$$

where $\epsilon_{0i} = \epsilon_{\infty(i-1)}$, and $\epsilon_{0i} - \epsilon_{\infty i} = \Delta\epsilon_i$ is the polarization strength of the ith range. The index i increases direction same as the frequency.

From the recent investigations [13], in the pure ice, the summations are dominated by the principal one term, intrinsic, or Debye dispersion relaxation whose parameters are usually described the characteristic of the ice.

Section 4 : Experimental Measurement

The impedance of the sample was measured as a function of frequency in the range 0.1 Hz to 100 kHz. In the frequency range of 50 Hz to 100 kHz measurements were performed with a General Radio type 1615-A Capacitance Bridge. In the low frequency range 0.1 Hz to 50 Hz, a specially designed bridge built around a GR type 1422CB precision capacitor was used. Temperature range of measurement was $-0.5\,^\circ$C to $-60.0\,^\circ$C.

4.1. Sample Cell

In this study, we developed the new three terminal sample cell. Fig 4.1 shows this sample cell, dimensions are incorrect. When cell is not of freeze need to measure. This cell includes the following items :

A: Higher electrode

B: Guarded electrode

C: Guard ring (spring-mounted)

D: Guarding rod for higher electrode

E: Thermocouple

F: Inner shield

G: Detail of inner shield showing that it is split to allow sample insertion. Only the back part (shown) is bolted onto the sample holder

H: Sample holder with heater connection block

I: Outer shield

J: Teflon insulation

K: Rod heater

L: Grounding screw

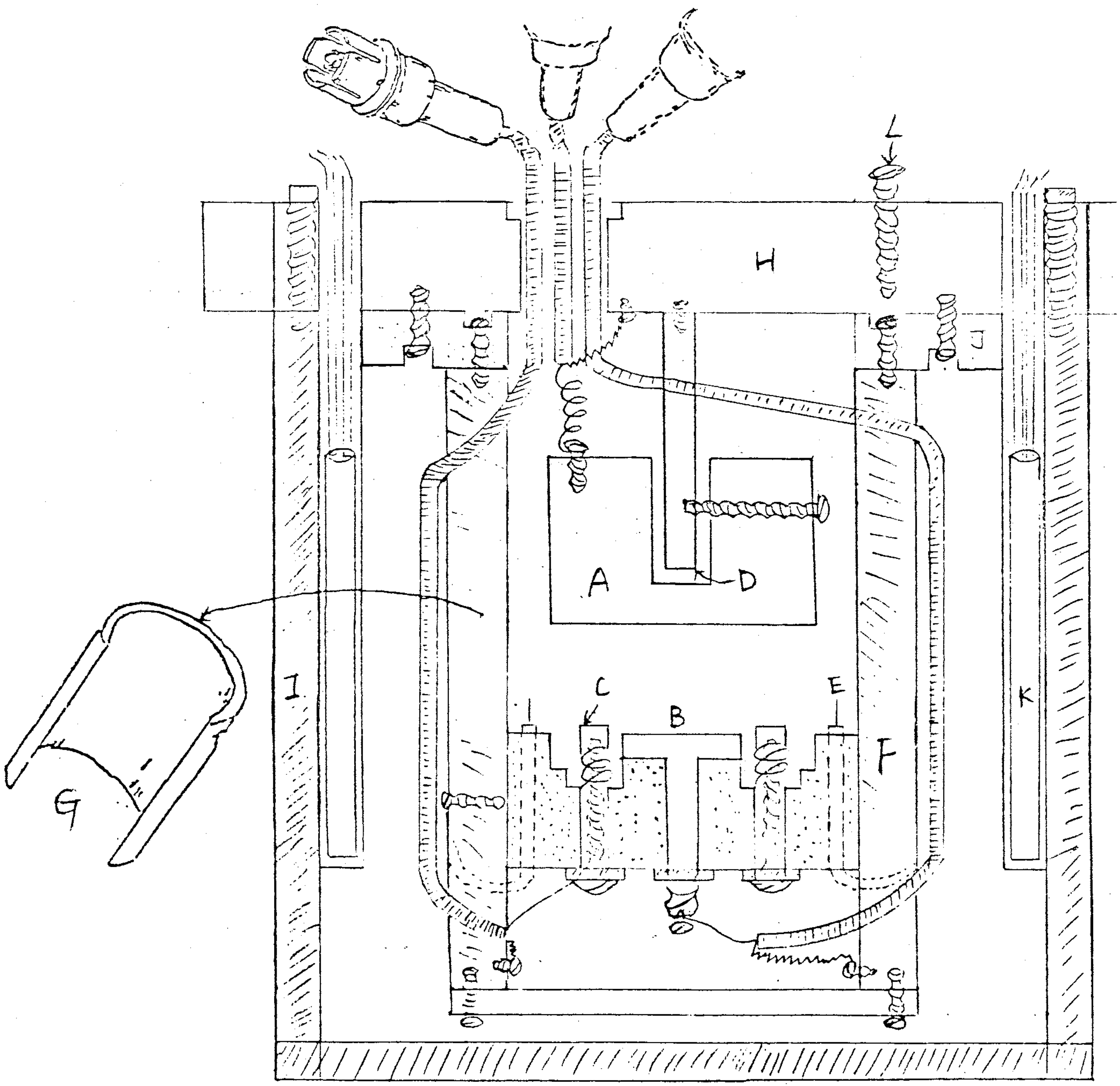


Fig. 4.1 Sample cell

4.2. The samples of ice

In this study, we use the following samples:

(1) Sample 185/90 : (A slice of ice column # 313-081 pure water). Fig. 4.2 shows the sample set in the sample cell.

Sample dimensions :

Diameter : 3.3 cm (estimated) Guard (reduce insulation difficulties, the guard frequently serves as an electrostatic shield of the collector; adequate shielding of the collector and the leads should be provided) and placed in the measuring cell (Fig. 4.2).

Sample thickness : $d_2 = 1.229 \pm 0.018$ cm

2 thin Teflon foils : $d_1 = 0.010$ cm (treated with silicone grease only on electrode)

$d_{total} = d_1 + d_2 = 1.239$ cm

Guarded center : $\frac{A}{l} = \frac{6.996}{1.239} = 5.646$ cm

$$C_g = \epsilon_0 \frac{A}{l} = (8.85 \times 10^{-14} \mathrm{F/cm})(5.646 \mathrm{cm}) = 0.50 \text{ pF}$$

$$C_\infty = (3.12) \times (0.50) \text{ pF} = 1.56 \text{ pF}$$

(2) Sample U185/90 : guard and center shunted by solid stainless steel disk. Fig. 4.3 shows the sample set in the sample cell.

Sample dimensions:

Diameter : 3.4 cm (estimated), so that $A = 9.079$ cm^2

Guard center : $\frac{A}{l} = \frac{9.079}{1.239} = 7.328$ cm

$$C_g = \epsilon_0 \frac{A}{l} = (8.85 \times 10^{-14} \mathrm{F/cm})(7.328 \mathrm{cm}) = 0.65 \text{ pF}.$$

$C_\infty = (3.12)(7.328)(8.85\times10^{-14}) = 2.02$ pF.

(3) Sample 185/112 = U185/90 : taken out of cell and electrodes replaced by 3-M foil guard electrodes. (Sample little or not affected by thermal cycling but when it was reintroduced into the cell after changing the electrodes, some melting occurred, this probably reduced the sample thickness. Total sample diameter is about 3.4 cm Sample dimensions are assumed identical to 185/90). Fig. 4.4 shows the sample set in the measuring cell.

Guarded center point : $\frac{A}{l} = 5.646$ cm

$$C_g = \epsilon_0 \frac{A}{l} = (8.85\times10^{-14}\text{F/cm})(7.328\text{cm}) = 0.50 \text{ pF}$$

$$C_\infty = (3.12)\times(0.50) = 1.56 \text{ pF}$$

(4) Sample 185/124 : pure ice, (nonnumbered slice of 313-081) 3-M foil Guard electrode. Fig. 4.5 shows the sample set in the sample cell.

Sample diameter : 3.3 - 3.4 cm (estimated)

Sample thickness : $d_2 = 1.138$ cm

Foil thickness : $d_1 = 0.017$ cm

$d_{total} = d_1 + d_2 = 1.155$ cm

Guarded center : $\frac{A}{l} = \frac{6.996\text{cm}^2}{1.155\text{cm}} = 6.057$ cm

$$C_g = \epsilon_0 \frac{A}{l} = (8.85\times10^{-14}\text{F/cm})(6.057\text{cm}) = 0.536 \text{ pF}$$

$$C_\infty = (3.12)\times(0.536)\text{pF} = 1.672 \text{ pF}$$

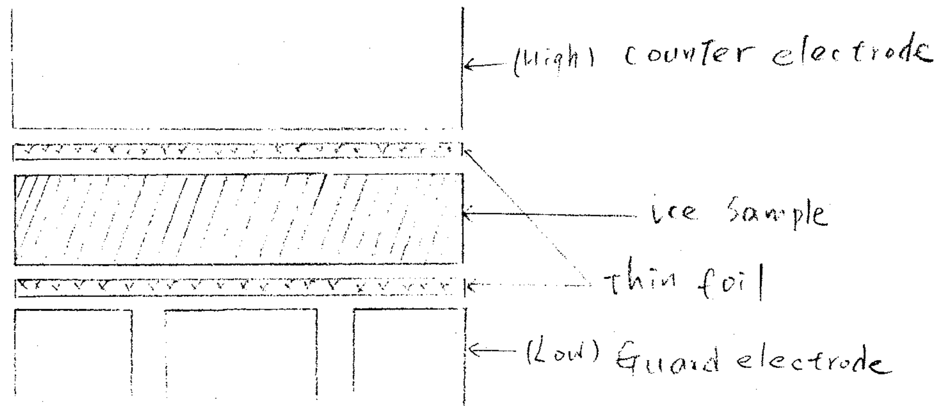


Fig. 4.2 Sample 185/90 arranged to the measuring cell

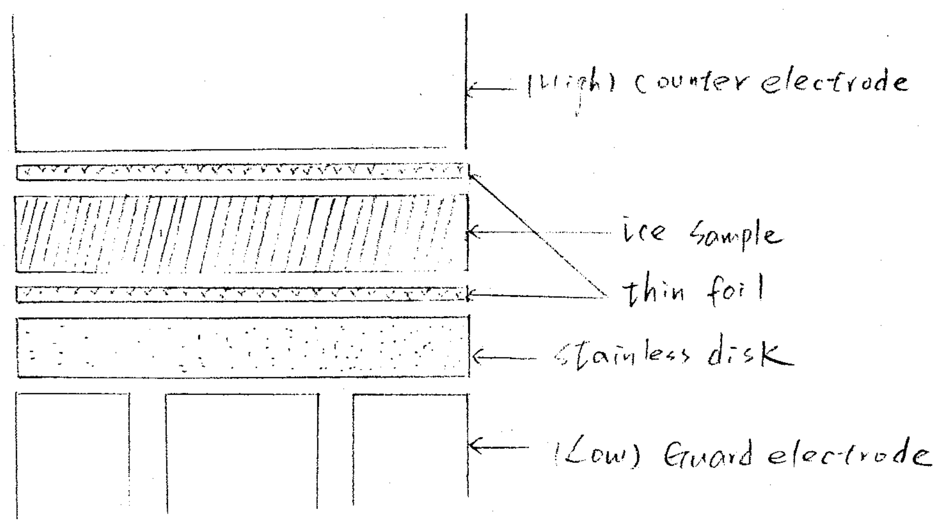


Fig. 4.3 Sample U185/90 arranged in the measuring cell

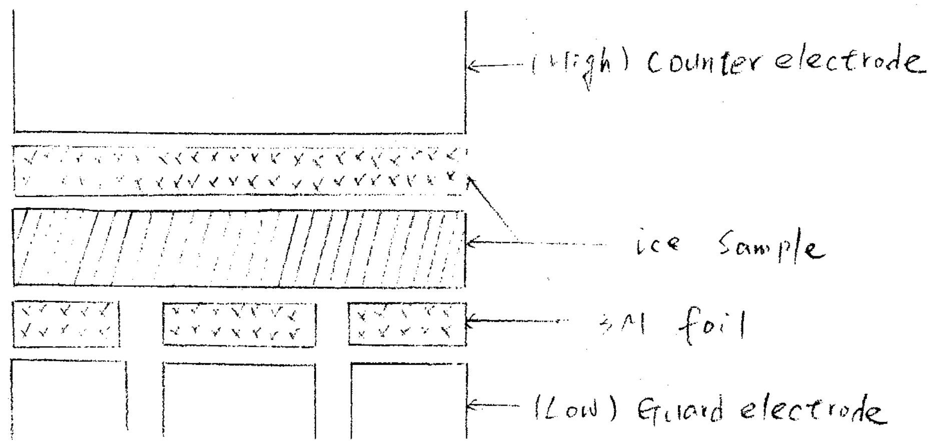


Fig. 4.4 Sample 185/112 arranged in the measuring cell

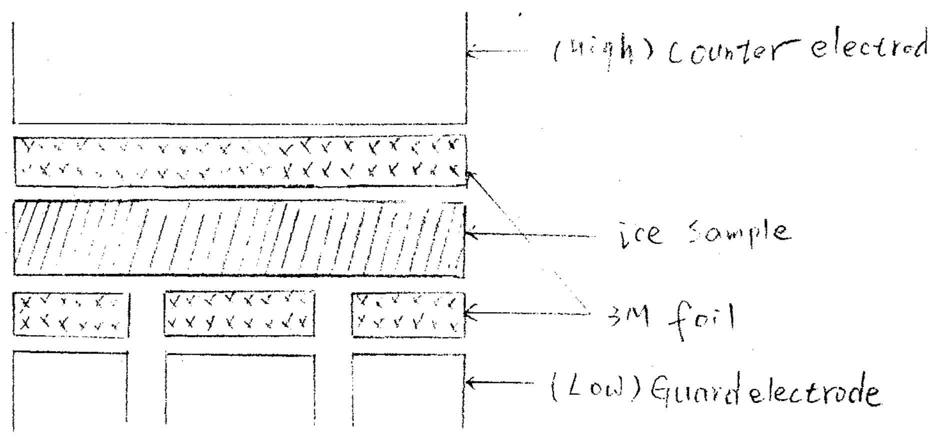


Fig. 4.5 Sample 185/124 arranged in the measuring cell

4.3. Experimental procedure

4.3.1 GR bridge

General procedure for making measurements with the 1615-A Capacitance bridge.

(1) Connect the sample to the GR bridge at the three terminal GR type connector labeled UNKNOWN (L and H).

(2) Connect the function generator from output channel A to the GR bridge at the BNC type connector labeled GENERATOR.

(3) Connect the null detector to the GR bridge at the GR type connector labeled DETECTOR.

(4) Connect the oscilliscope to the function generator from one of the outputs of the function generator, usually channel A which is the same output that is connected to the GR bridge.

(5) Connect the frequency counter to the function generator from one of the outputs of the function generator, usually channel B.

(6) Turn the function generator on with the red power button.

(7) Turn the frequency counter on with the red power button (for these frequencies the Gate should be set at 10's and the sensitivity should be at 0.02).

(8) Turn the oscilliscope on with the black power button (If the TEKTRONIX 2213 is being used the button is located next to the bottom right of the screen).

(9) If there is a noise signal on the oscilliscope when no voltage is being sent from the function generator, check to be sure that all the machines are connected to the same ground.

(10) Adjust the frequency dial on the function generator to the desired frequency.

(11) Adjust the frequency on the null detector to the same frequency as on the function generator.

(12) Increase the voltage with the amplitude knob on the function generator to the limiting voltage corresponding to the frequency being used (i.e. at 50 Hz use 1.5 volts, at 100 Hz use 3 volts, at 1 kHz use 30 volts).

(13) Turn the null detector on with the gain switch. As the gain is increased, the needle on the null detector will increase away from zero. With the needle at about midway between zero and offscale on the dial, begin adjusting the capacitance and conductance/dissipation knobs. To achieve the most accurate reading, increase the gain as the measurements minimize the dial reading. When the gain is adjusted to its highest sensitivity and the capacitance and conductance/dissipation knobs have given the lowest value on the null detector (i.e. zero), then the minimum has been achieved. A record of this capacitance and conductance/dissipation should be made.

Very often the gain introduces fluctuations in the needle's position making accurate readings very difficult. One way to lessen these fluctuations is to decrease the gain until the needle is stable again. Hopefully, this occurs before the off position on the gain switch. Fig. 4.6 shows block diagram of equipment arrangement in this procedure.

4.3.2 Low frequency bridge

General procedure for making measurements with the low frequency bridge (LF bridge).

(1) Connect the sample to the low frequency bridge at the GR type connectors labeled SAMPLE HOLDER.

(2) Be sure that the variable capacitor is connected to the low frequency bridge at the GR type connectors labeled VARIABLE CAPACITOR.

(3) Connect the function generator from the output at channel A to the high voltage amplifier at the BNC type connector labeled INPUT.

(4) Include two parts:

  a. Connect the oscilliscope to the function generator from one of outputs of the function generator, usually channel A. This is the same as the output connected to the LF bridge.

  b. Connect the other channel of the oscilliscope to the LF bridge at the BNC type connector labeled output.

(5) Be sure that the DETECTOR is connected to the bandpass amplifier INPUT in the LF Bridge network. This is also a GR type connection.

(6) Connect the frequency counter to the function generator from one of the outputs of the function generator usually channel B.

(7) Turn the function generator on with the red power button.

(8) Turn the frequency counter on with the red power button (For these frequencies the Gate should be set at .1s with the GREEN BUTTON pushed in for period (out is frequency) and the sensitivity at 0.02 Vrms).

(9) Turn the high voltage amplifier on with the toggle switch. The orange light will turn on. Be sure the gain is set to one (the lowest of the 3 positions).

(10) Turn the bandpass amplifier on with the toggle switch. A green light will appear.

(11) Be sure the pre-amplifier switch is below 1 before inputting any voltage from the function generator. Also the Q switch should be set to 10.

(12) Set Range Select for appropriate capacitance range on the variable capacitor (i.e. if the blocking capacitance is 150 pF, then the range select should be at 1.0; if the blocking capacitance is less than 100 pF, then 0.1 can be used; if it is less than 10 pF, then 0.01 can be used).

(13) Set the GR dial so that the CD dial reading is between 0 and 999.9 (preferably greater than 100). Often the GR setting cannot be established until the minimum is approached by adjusting the variable capacitance and the CD (conductance dial) and observing a reasonably straight line on the oscilliscope.

(14) Set the frequency on the function generator to the desired frequency between 50 and 0.1 Hz.

(15) Set the filter on the LF bridge to the same frequency as in (14). If the frequency is not on the filter dial of the bridge, move the filter switch to the out position.

(16) input the appropriate voltage for the corresponding frequency from the function generator (i.e. at 50 Hz use 30 volts).

(17) Turn the pre-amplifier switch to 1 and begin balancing the ice sample by adjusting the CD dial and the variable capacitance. As frequency is decreased the response of the oscilliscope is retarded so wait patiently between adjustments to either the CD dial or the variable capacitor.

(18) As a minimum is approached, sensitivity can be increased by turning the pre-amplifier to 10, 100 and/or 1000 and the Q dial to 100.

(19) For frequencies below 1 Hz, the inputs to the oscilliscope are transferred to the Chart Recorder. The function generator output is usually connected to the purple pen and LF bridge output is usually connected to the red pen. A maximum input voltage of 10 volts is recommended. The FINE and COURSE dials on the pre-amplifier adjust the zero position of the red pen (bridge output). Fig. 4.7 shows block diagram of equipment arrangement in this procedure.

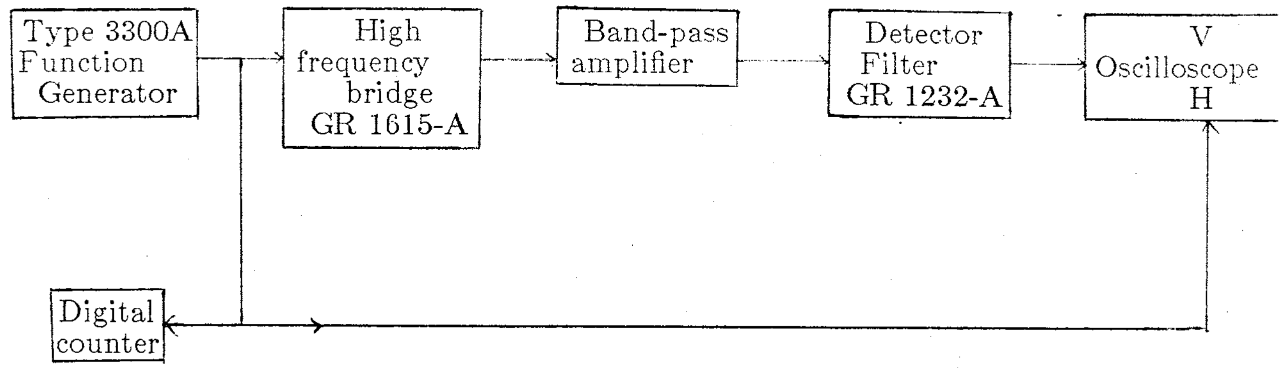


Fig. 4.6 Block diagram of equipment arrangement used with the high frequency bridge.

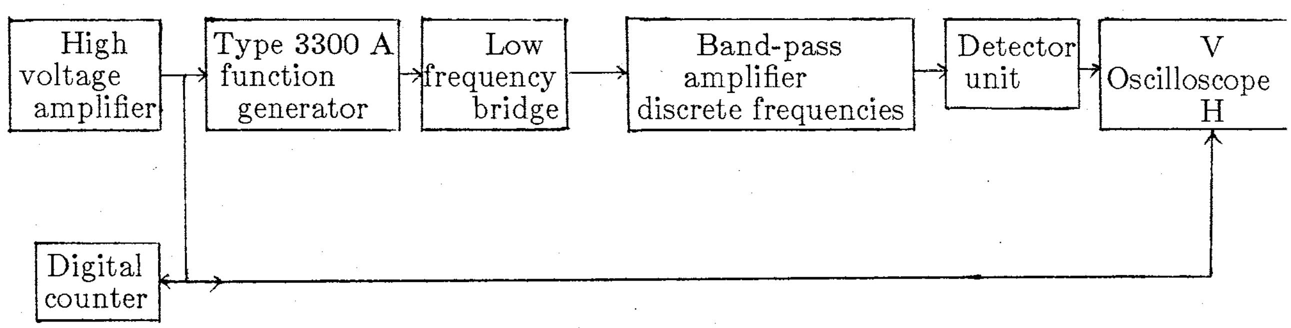


Fig. 4.7 Block diagram of equipment arrangement used with the low frequency Bridge.

Section 5 : The Mathematical Model

5.1 Equivalent Circuit

The mathematical model representing electrical properties of ice is derived from an electrical circuit model which has been successfully used for the analysis of dielectric relaxation spectra in both pure and doped ice (Fig. 5.1). Representation of Debye response by a series combination of one capacitance and one resistance has been well established (v. Hippel, 1954). Pure ice has one known Debye mechanism, the principal relaxation, associated with reorientation of polar molecules in an electric field. It is represented by the series combination C_1 , G_1 in Fig. 5.1. A second Debye relaxator has been included in the equivalent circuit (Fig. 5.1) to cover unspecified "anomalies" of the electrical behavior of ice (e.g. : point defects associated with dislocations, surface roughness, electrode effects). Inclusion of a second element will yield a closer fit of model parameters to experimental data. Comparison of results obtained by fitting with one or two Debye elements may yield useful information about ice relaxation mechanism. The single-element procedures are much more efficient for computation.

A dc conductance, G_0, is needed to describe effects of free charge carriers in ice. C_I is the high-frequency limiting capacitance of the dispersion representing electronic polarization. The driving capacitance, C_0, represents the effective aggregate capacitance of the blocking foils.

Table I lists the symbols used in the equivalent circuit diagram. Table II shows those used in the derivation of the circuit response and their equivalents in the program listings. Table III shows the two scaling schemes that can be used with the algorithms.

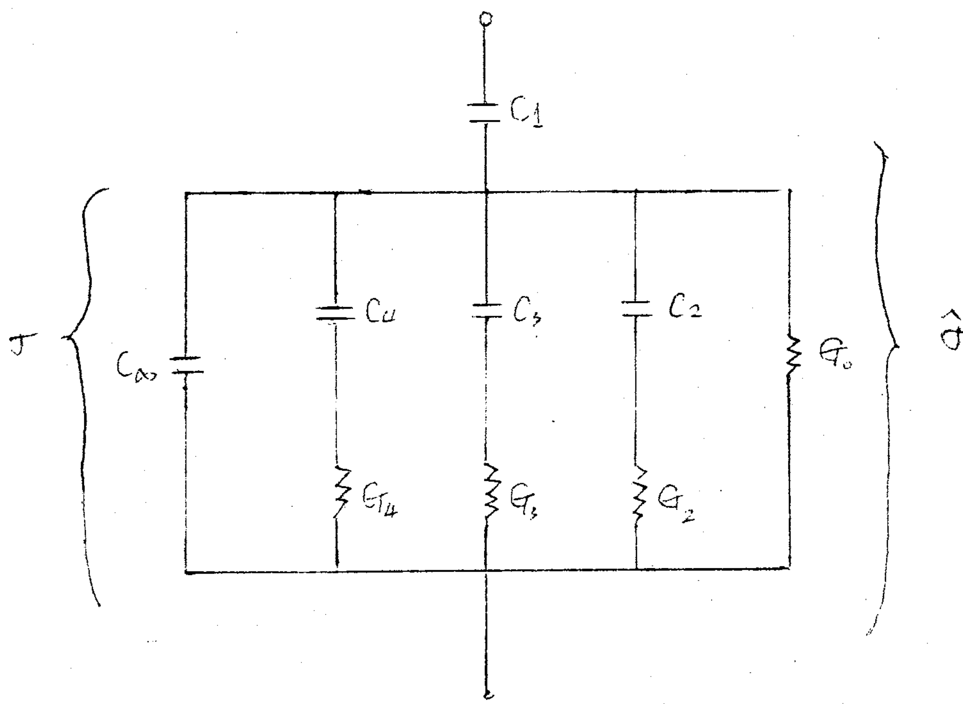


Fig. 5.1 Equivalent circuit

Table I. Equivalent Circuit Elements and Associated Parameters

Symbol	Significance	Defining relation	[Units]
C_0	Driving (=blocking layer) capacitance	$C(\omega\ 0)$	[pF]
C_I	Limiting high-frequency capacitance	$C(\omega\ \infty)$	[pF]
G_0	DC conductance	$G(\omega\ 0)$	[μ S]
C_1, C_2	Equivalent capacitances of Debye relaxations	$\tau = C/G$	[pF]
G_1, G_2	Equivalent conductances of Debye relaxations	$\tau = C/G$	[μ S]
τ_1, τ_2	Debye relaxation times	$\tau = C/G$	[ms]
C_g	Geometrical capacitance of sample holder	$\epsilon_{\hat{\nu}} \frac{A}{L}$	[pF]

Table II. Correspondence of symbols used in response analysis (Sec 5, 6) and computer listings. Where applicable, scaling alternative A1 is implicit.

Response analysis (Sec 5, 6)	Significance or defining equation	Listings	Notes
α_1,α_2	6.1a,b	C1,C2	
$\beta_1,\beta_2,\beta_3,\beta_4$	6.3a,b,c,d	G1,G2,G3,G4	
r	6.2	R	
T_1, T_2	5.2a	T1, T2	
$1/T_1$, $1/T_2$	5.2b	F1, F2	
F_0	5.2c	F0	
C_0	Blocking capacitance	E0	
C_1, C_2	Debye relaxation capacitances	E1, E2	
C_I	Limiting h.f. capacitance	EI	Subroutine PAR
B_1, B_2	B_1=E_1T_1, etc	B1, B2	Subroutine PAR
X	5.4c	X	
Y	5.4d	Y	
p	5.3a	P	
q	5.3b	Q	

Table III Scaling

Quantity	Symbol	Scaling A1	A2
Input data			
Parallel capacitance	$C_p(\omega)$	pF	dimensionless
Parallel conductance	$G_p(\omega)$	μ S	krad—s^{-1}
Series capacitance	$C_s(\omega)$	Convert to C_p (program DIEL) prior to inputting in fitting programs.	
Dissipation factor	D	Convert to G_p (program DIEL) prior to inputting in fitting programs.	
Limiting h.f. capacitance	C_I	pF	dimensionless ($\epsilon_\infty = 3.12$)
Frequency	f	kHz	kHz
Geometric factor (parallel plate capacitor)	A/L	cm	cm
Output			
Layered capacitor	Symbol	A1	A2
Spectrum			
real part	$X(\omega)$	pF	Dimensionless *
imaginary part	$Y(\omega)$	pF	Dimensionless *
Blocking capacitance	C_0	pF	Dimensionless
Bulk ice	Symbol	A1	A2
Spectrum			
real part	$P(\omega)$	pF	Dimensionless *
imaginary part	$Q(\omega)$	pF	Dimensionless *
AC conductance	FQ	nS	krad—s^{-1}
Bulk ice parameters	Symbol	A1	A2
Polarization strengths	E1, E2, EI	pF	Dimensionless
Relaxation frequencies	F1, F2**	kHz	kHz
Relaxation times	T1, T2**	ms	ms
DC conductance (conductivity)	F0	pF	$(ms)^{-1}$
Conversion	Symbol	A1	A2
Relaxation times	τ_1, τ_2 [s]	$\frac{T}{2\pi}10^{-3}$	$\frac{T}{2\pi}10^{-3}$
DC conductivity	$\sigma_0[Scm^{-1}]$	$\frac{(2\pi)(F0)(10^3)}{A/L}$	$(2\pi\epsilon_v)(F0)(10^3)$***

* Symbols ϵ' , ϵ'' are customarily used for the real and imaginary parts, respectively.

** $T_1 = F_1^{-1}$ etc. It follows that $F_1 T_1 = 1$ etc, and $T = 2\pi\tau$.

*** $\epsilon_{\hat{\nu}} = 8.85 \times 10^{-14} [F-cm^{-1}]$ (permittivity of free space, usually symbolized by ϵ_0).

5.2 Derivation of circuit response

The complex admittance of bulk ice in the test capacitor

$$\sigma = G_0 + j\omega C_\infty + \frac{j\omega C_1}{1+j\omega\tau_1} + \frac{j\omega C_2}{1+j\omega\tau_2} \tag{5.1}$$

The effective response of the test capacitor is

$$\hat{\sigma} = \frac{j\omega C_0 \sigma}{j\omega C_0 + \sigma} \tag{5.2}$$

Now let :

$$T_1 = 2\pi\tau_1$$

$$\omega\tau_1 = fT_1 \ ,$$

and similarly for T_2. Furthermore

$$F_0 = \frac{G_0}{2\pi}$$

and

$$\frac{\sigma}{j\omega} \equiv p - jq \qquad \frac{\hat{\sigma}}{j\omega} \equiv X - jY,$$

where p, q are normalized susceptance and loss factor of the ice sample, and X, Y those of the test cell.

Separating real and imaginary parts of the ice response

$$p = C_\infty + \frac{C_1}{1+f^2T_1^2} + \frac{C_2}{1+f^2T_2^2} \tag{5.3a}$$

$$q = \frac{F_0}{f} + \frac{C_1 fT_1}{1+f^2T_1^2} + \frac{C_2 fT_2}{1+f^2T_2^2}. \tag{5.3b}$$

Important transformations are

$$p = \frac{C_0[(C_0-X)X-Y^2]}{(C_0-X)^2+Y^2} \tag{5.4a}$$

$$q = \frac{C_0^2 Y}{(C_0-X)^2+Y^2} \tag{5.4b}$$

$$X = \frac{C_0[(C_0+p)p+q^2]}{(C_0+p)^2+q^2} \tag{5.4c}$$

$$Y = \frac{C_0^2 q}{(C_0+p)^2+q^2} \tag{5.4d}$$

Note that as $f \longrightarrow 0$, $q \longrightarrow \infty$, while $Y \longrightarrow 0$, and $X \longrightarrow E_0$. as has been discussed elsewhere (Gross et al., 1980).

5.3 A note on scaling and symbols used in this report

It is customary to scale (normalize) the complex dielectric response by separating it into real and imaginary components and then dividing by (ωC_g), where C_g is the geometrical capacitance of the test cell without its dielectric filling (e.g. : von Hippel, 1954, p. 88). The identical result is achieved by multiplying Eq. (5.2) with $(j\omega C_g)^{-2}$ and then proceeding to separate real and imaginary parts. The resultant equations are in terms of dimensionless relative polarization strengths (the sum of which is the relative permittivity), a dc conductivity parameter ($\sigma_{DC}/\omega\epsilon_\nu$) with dimension T^{-1}, and relaxation times (independent of scaling method). This scaling method is henceforth called Alternative 2 (A2). In order to apply this method (A2), it must be assumed that the dielectric is homogeneous and completely fills the test cell (i.e. test cell and dielectric have the same geometry).

In the measurements discussed in this report, the sample cell contains a layered dielectric of the Maxwell-Wagner type (von Hippel, 1954, p. 228-230; Gross et al., 1980), with each dielectric having its own geometry, different from each other and from the test cell. Moreover, space-charge effects can add still other "layers" (each layer being characterized by its capacitance and conductance). For all these reasons and following a recommendation of Macdonald (1976, p. 166-167) we deem it advisable to normalize for sample geometry only after ice bulk parameters have been extracted from the dielectric response spectrum. Initial scaling, therefore, does not involve C_g. This method, Alternative 1 (A1), has been used in the derivations of sections 5 and 6.

It can be shown that the term F_0, the normalized dc conductance, has the dimensions of capacitance (picofarads) with Alternative 1, and of frequency (kHz) with Alternative 2. Scaling relations are summarized in Table III.

Our programs admit data of either type of normalization and give correct results if the units specified in Table III are used for input data. Table IV lists the principal equations and their respective appearance in A1, A2, and computer listings.

Table IV Defining equations in three forms

Equation	A1	A2	Algorithm
5.3a	$p = C_\infty + \frac{C_1}{1+T_1^2f^2} + \frac{C_2}{1+T_2^2f^2}$	$p^* = \epsilon_\infty + \frac{\epsilon_1}{1+T_1^2f^2} + \frac{\epsilon_2}{1+T_2^2f^2}$	$P = E_I + \frac{E1}{1+C1F^2} + \frac{E2}{1+C2F^2}$
5.3b	$q = \frac{F_0}{f} + \frac{C_1T_1f}{1+T_1^2f^2} + \frac{C_2T_2f}{1+T_2^2f^2}$	$q^* = \frac{\sigma}{\omega\epsilon_\nu} + \frac{\epsilon_1T_1f}{1+T_1^2f^2} + \frac{\epsilon_2T_2f}{1+T_2^2f^2}$	$Q = \frac{F0}{F} + \frac{E1FT1}{1+C1F^2} + \frac{E2FT2}{1+C2F^2}$
5.4a	$p = \frac{C_0[(C_0-x)x-y^2]}{(C_0-x)^2+y^2}$	$p = \frac{\epsilon_0[(\epsilon_0-x)x-y^2]}{(\epsilon_0-x)^2+y^2}$	$P = \frac{E0[(E0-X)X-Y^2]}{(E0-X)^2+Y^2}$
5.4b	$q = \frac{C_0^2y}{(C_0-x)^2+y^2}$	$q = \frac{\epsilon_0^2y}{(\epsilon_0-x)^2+y^2}$	$Q = \frac{E0^2Y}{(E0-X)^2+Y^2}$
5.4c	$X^{**} = \frac{C_0[(C_0+p)p+q^2}{(C_0+p)^2+q^2}$	$X^{***} = \frac{\epsilon_0[(\epsilon_0+p)p+q^2]}{(\epsilon_0+p)^2+q^2}$	$X = \frac{E0[(E0+P)P+Q^2]}{(E0+P)^2+Q^2}$
5.4d	$Y^{**} = \frac{C_0^2q}{(C_0+p)^2+q^2}$	$Y^{***} = \frac{\epsilon_0^2q}{(\epsilon_0+p)^2+q^2}$	$Y = \frac{E0^2Q}{(E0+P)^2+Q^2}$

* Customarily $\epsilon'(\omega)$, $\epsilon''(\omega)$.

** Use p, q defined for A1 (Table III).

*** Use p, q defined for A2 (Table III).

Section 6 : Approach to Fitting

Our purpose is to estimate ice parameters, C_1 , T_1 , C_2 , T_2 and G_0 from measurements representing the complex response, $\hat{\sigma}$, of the test cell. To accomplish this, it is necessary also to estimate C_0 . C_∞ is invariant and known.

Measurements of the two elements of $\hat{\sigma}$ are made over a set of frequencies on a sample of ice at a constant temperature. Our base for a parameter estimate is a set of data values $\{ (f_i , X_i , Y_i) ,\ i = 1, n \}$.

6.1 Fitting in the f, p, q domain

Parameter fitting in the (X,Y) domain requires a "nonlinear" procedure because the relations (Eqs. 5.4a, b) involve the parameters in a nonlinear form. Such procedures are iterative in nature and may require good starting estimates. To avoid these problems, our new approach is fitting of parameters in the p or in the q domain. The expressions for p and q are rational in the parameters. The relations can be transformed into relations which are linear in an equivalent set of parameters. Direct (non-iterative) solutions for parameters can be made.

Theoretically, if data are consistent with the model, parameters can be determined either in the p- or in the q-domain. Early fitting was done in the q-domain. In the presence of dc conductance, the variable q is unbounded as $f \rightarrow 0$ (Eq. 5.3b); fq is bounded and was chosen as the fitted variable. For two Debye elements, the fq fit involves the five ice parameters C_1 , T_1 , C_2 , T_2 , and F_0. The fq results were not satisfactory. This is attributed, at least in part, to the fact that $fq \rightarrow 0$, as $f \rightarrow 0$, so that at low frequencies the effect of small measurement errors can be serious. Fitting in the q-domain was terminated. Simultaneous fitting in p and q, as proposed by Macdonald and Garber (1977) [14] was not attempted.

The p relation involves the four Debye parameters C_1, T_1, C_2, T_2, if two Debye elements are chosen for the model.

$$p = \frac{C_1}{1+f^2T_1^2} + \frac{C_2}{1+f^2T_2^2} + C_\infty. \tag{5.3a}$$

Let

$$\alpha_1 = T_1^2 \tag{6.1a}$$

$$\alpha_2 = T_2^2 \tag{6.1b}$$

$$r = p - C_\infty. \tag{6.2}$$

Eq. (5.3a) can be cleared of fractions and restated

$$\beta_1 + \beta_2 f^2 - \beta_3 r f^2 - \beta_4 r f^4 = r \tag{6.3}$$

wherein :

$$\beta_1 = C_1 + C_2 \tag{6.3a}$$

$$\beta_2 = C_1\alpha_2 + C_2\alpha_1 \tag{6.3b}$$

$$\beta_3 = \alpha_1 + \alpha_2 \tag{6.3c}$$

$$\beta_4 = \alpha_1\alpha_2. \tag{6.3d}$$

Eq. (6.3) is linear in the β-coefficients.

Given a data set

$$\{ (f_i , p_i), i = 1, n \}$$

calculate

$$r_i = p_i - C_\infty, \qquad i = 1, n.$$

At this point, two alternative methods may be used to extract Debye parameters C_1 , T_1 , C_2 , T_2, a point-fit method or a least-squares method.

6.2 Point fit

If four data points are chosen (n=4), the β-coefficients can be calculated from the four linear equations obtained by substituting the data points into Eq. (6.3). The procedure is outlined in Appendix D.

6.3 Least-squares

It may be preferable to use a larger set of data points and a least-squares fitting procedure to evaluate β-coefficients.

Our least-squares procedure is not weighted. It minimizes the sum of squares of the p-residuals (the difference between p-values calculated from the parameters and from the experimental data, respectively). In practice, some weighting is done in choosing the data set. A weighting study may be desirable for some applications.

6.4 Evaluation of parameters

Whether using a point-fit or least-squares algorithm, the ice parameters are calculated from the β -values :

$\alpha_1+\alpha_2 = \beta_3$; $\alpha_2 = \beta_3-\alpha_1$

$\alpha_1\alpha_2 = \beta_4$, so that

$$\alpha_1^2-\beta_3\alpha_1+\beta_4 = 0. \tag{6.6}$$

Test results have shown that, for ice, $|\alpha_1| >> |\alpha_2|$ in general. The larger solution of the quadratic equation (6.6) is chosen as α_1

$$\alpha_1 = \frac{\beta_3}{2}+\sqrt{(\frac{\beta_3}{2})^2-\beta_4} \tag{6.6a}$$

$$\alpha_2 = \beta_3-\alpha_1$$

$$T_1 = \sqrt{\alpha_1}; \quad T_2 = \sqrt{\alpha_2} .$$

$$C_1 = (\beta_2-\alpha_2\beta_1)/(\alpha_1-\alpha_2)$$

$$C_2 = \beta_1 - C_1.$$

If α_1 is complex (6.6a), the experimental data are not fully consistent with the model. If the imaginary term of α_1 is much smaller in absolute value than the real term, a single Debye element is implied, $C_2 = 0$. Parameters of that element are approximated by

$$C_1 = \beta_1, \quad \alpha_1 = \beta_3/2, \quad T_1 = \sqrt{\alpha_1}\,.$$

For fitting in such cases, use of a single Debye element procedure is preferred.

For a single Debye element model

$$\frac{C_1}{1+\alpha_1 f^2} = p - C_\infty = r.$$

Clearing of fractions and rearranging

$$C_1 - \alpha_1 r f^2 = r,$$

a linear relation in C_1 and α_1. Point fit estimates of C_1 and α_1 can be made using two data points, or least-squares estimates using a larger set of points.

6.5 Estimate of C_0

A close estimate of C_0 is needed for accurate computation of the ice response from the test-capacitor response (Eqs. 5.4a,b). Significance loss (see section 6.8) occurs in calculating p-values from X and Y data values, especially at low frequencies. Values of p and of the parameter estimates are highly sensitive to changes of C_0. The mathematical condition is

$$\omega \longrightarrow 0, \; X(\omega) \longrightarrow C_0. \tag{6.7}$$

At sufficiently low measurement frequencies, C_0 can be extrapolated graphically from the Cole-Cole plot. This condition obtains when the lowest frequency measurement point is located very close to the real (C) axis of the Cole-Cole plot.

Sometimes, however, this point has to be deleted because of measurement inaccuracy. In this case, a mathematical method is necessary. Several approaches were tried for estimating C_0; three of these will be discussed.

6.5.1 Least-squares approach. A least-squares procedure was developed which attempts to determine the value of C_0 that minimizes the sum of squares of the p-residuals. This procedure worked well when a well-defined minimum existed, but it failed on many data sets, especially measurements at low temperature. Scan runs to tabulate residuals as a function of C_0 showed multiple minima, such that the procedure could not be reliable. Measurement bias is a possible cause of poor results. With data sets on which the procedure worked, the C_0 value obtained varied with the choice of data points and in particular was affected by the high-frequency cutoff chosen. When the data do not fit the model well, there is no assurance that the least-squares method produces an unbiased estimate of C_0; the evidence suggests otherwise. This procedure was discarded.

6.5.2 Point-fit approach. A second procedure takes advantage of the sensitivity of p-residuals to changes in C_0. It estimates C_0 by zeroing the sum of a few low-frequency p-residuals. Two initial estimates of C_0 are calculated using 2-point and 3-point rational approximations of X as a function of frequency (identical to the 2-point and 3-point extrapolations discussed later). A classical secant method then is used to determine C_0, iterating until the C_0 corrections fall within a specified cutoff tolerance, or at 8 iterations, whichever is smaller. Let r designate the sum of p-residuals which is a function of C_0: $r = r(C_0)$. Given two data points (C_0, r), a secant line is used to calculate an error estimate, say d_n, for the last $C_{0,n}$, where n is an iteration index. Then $C_{0,n+1} = C_{0,n} - d_n$. Data are printed at each step to confirm convergence (decreasing magnitude of d_n) or failure to converge. This procedure usually is reliable in finding an estimate of C_0. It is susceptible to data errors at low frequency. Data errors are amplified by significance loss; low-frequency residuals often are highly erratic. Low-frequency measurement bias will cause bias in the estimate of C_0 and poor estimates of parameters. If y (dissipation) values are affected by loss mechanisms not included in the model, the estimate of C_0 may be biased.

6.5.3. Extrapolation. The third procedure is the simplest, most efficient, and most reliable of the three. It extrapolates low-frequency X-values to obtain an estimate of C_0 (Eq. 6.7). Values of Y are not involved. From circuit theory, X is an even function of f. In our application, rational approximations of X(f) at small f are more accurate for extrapolation than polynomials. Three point-fit extrapolation procedures for C_0 were developed.

$$\text{Two point} \quad : \quad X2(f) = \frac{C_0}{1+af^2}$$

$$\text{Three point} : \quad X3(f) = \frac{C_0+af^2}{1+bf^2}$$

$$\text{Four point} \quad : \quad X4(f) = \frac{C_0+af^2}{1+bf^2+cf^2}.$$

The coefficients in these expressions are generic and change with the expressions. The relations can be cleared of fractions to obtain relations linear in the coefficients. The set of linear equations obtained by substituting the appropriate number of data points in the relations is solved for C_0.

The optimal choice of an extrapolation depends on the particular data set. The considerations involved are the accuracy of the data measurements and the differences in the X-values of the points used for extrapolation. Measurement errors are amplified in the extrapolations, the amplification increasing with the number of data points used. Low-order extrapolation is preferable when measurement error is of the same range as X-differences, and high order extrapolation when X-differences are relatively large. The four-point extrapolation is needed for old low-temperature data. With better low-frequency data from the new bridge, only two- or three-point extrapolation is needed.

This third procedure requires only a single evaluation of the Debye parameters.

6.6 Estimate of F_0

The ice conductivity parameter, F_0 is calculated from q-values (Eq. 5.3b). A value $f_0(i)$ is calculated at each data point, and the average value designated F_0. Because of significance loss in the tails, this should be calculated from the frequency range around the principal dispersion frequency (see below).

$$F_0(i) = FQF - \left\{ \frac{E1T1}{1+F_{(i)}^2 C1} + \frac{E2T2}{1+F_{(i)}^2 C2} \right\} F_{(i)}^2 \tag{6.8}$$

where

$$FQF = \frac{E0^2 FY}{(E0-X)^2+Y^2} = fq,$$ (from Eq. 5.4b), computed from measured values of X and Y.

6.7 Parameter estimates : additional considerations

For the evaluation of all parameters other than C_0, best accuracy of estimates is obtained with restricted range of data. Let $f_1 = 1/T_1$, the relaxation frequency of the principal Debye element. An approximate range of frequencies between $f_1/2$ and $2f_1$ will cover the frequency range of large changes of the principal element. Inclusion of the data "tails" may contribute errors from extraneous factors such as significance loss (see below), weighted into the estimates by the "tails". High density of frequencies requires excessive data taking and computer time. Eight or so data points should be sufficient for good accuracy estimates of parameters while retaining the ability to detect data anomalies. The critical frequency range depends on temperature and is selected from a Cole-Cole plot of the complete data set.

At this time we are using the second Debye element only for the purpose of improving the fit of the principal element. The physical meaning of this second element (e.g.: extrinsic effects due to dislocations, surface roughness effects, etc.) remains an object for study.

6.8 Significance loss

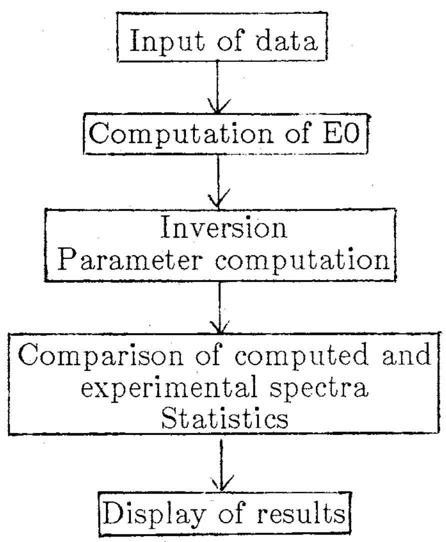
Significance loss occurs in calculating the difference of two numbers which are almost the same in value. The difference has fewer significant figures than the given numbers. When there is error in the numbers differenced, the relative error in the difference often is much larger than the relative errors of the given numbers. Significance loss is the principal cause of errors in computed results. In calculating p-values from data, the differences C_0–X (Eqs. 5.4a,b) have large significance loss at low frequencies. An accurate value of C_0 is critical for accuracy in the desired parameters.

Another problem of significance loss occurs in the determination of F_0 (Eq. 5.3b) at both the high and the low ends of the frequency range.

As discussed elsewhere (Gross and Johnson, 1983) the effect of significance loss is most serious in the principal polarization strength, the least serious in the relaxation times. This is so because over the temperature range of interest, relaxation times change by orders of magnitude whereas polarization strength only by a factor of two or three.

6.9 Inversion scheme. General outline

Programs used for the inversion of ice measurements made in a blocking capacitor follow the general pattern shown below. For maximum flexibility, the programs are built up of modular subprograms and subroutines that can be combined in various ways for different fitting strategies, as outlined earlier. Subroutines are described in App. C, and the various programs are detailed in App. D and E.



Section 7 : Interpretation and Discussion

7.1 Interpretation

The dielectric parameters were determined by measurements (Section 4). Limiting conductivities, relaxation times, and polarization strengths of partly overlapping ranges were computed from linearized plots of the Debye equation. It was assumed that dielectric relaxation in ice can described by a small number of discrete relaxation ranges, exclusive of space-charge ranges, each characterized by a single relaxation time.

In this study used Teflon foil as blocking electrodes [15], so that calculation was required to extract the parameters of bulk ice from the calculated values [16, 17]. The principal relaxation time and principal dielectric conductivity of a number of samples of pure ice measured as a function of temperature either with stainless-steel guard electrodes or with blocking electrodes showed agreement with the data published by Auty and Cole (1952) [18]. The straight lines described by Auty and Cole's data for the principal relaxation time, and for the principal dielectric conductivity.

7.1.1 Evaluation of dispersion

The impedance Z is giving by the two bridge readings Gp and Cp according to the defining formula

$$\frac{1}{Z} = \mathrm{Gp} + i\omega \mathrm{Cp}, \tag{7.1}$$

which correspond to a parallel equivalent circuit. The raw data Gp and Cp are proportional to the conductivity σ and to the dielectric constant ϵ respectively. For the case where the dispersion is a Debye dispersion with a single relaxation time, the plot Gp versus Cp forms a straight line whose end points are giving by (G_0 , C_s) and (G_∞ , C_∞) [19, 20, 21]. The quantities in the brackets represent the limiting values of Gp and Cp at low and high frequency respectively.

In this study we set our samples are two Debye elements, in Fig. 7.1 series still fulfill this linear relationship quite well. Additional dispersion regions appear as deviations at the ends of the line. Fig. 7.1 shows as an example a plot of the dispersion curve. In the low-frequency region the conductivity is affected only to a small extent by the extra dispersion. The limiting value G_0 can therefore easily be determined. When G_0 is known, C_s can be determined from the plot of Gp versus Cp as shown in Fig. 7.1 series; Fig. 7.1(a) Evaluation of dispersion parameters for pure ice at -10.2 ° C (sample 185/90 III), Fig. 7.1(b) Enlarge the low frequency part. From the Fig. 7.1(b) we can estimate the C_0 then we can do the normalized Cole-Cole plot. Fig. 7.2(a) shows the Cole-Cole plot, Fig. 7.2(b) shows normalized Cole-Cole plot for pure ice at -10.2 ° C (sample 185/90 III).

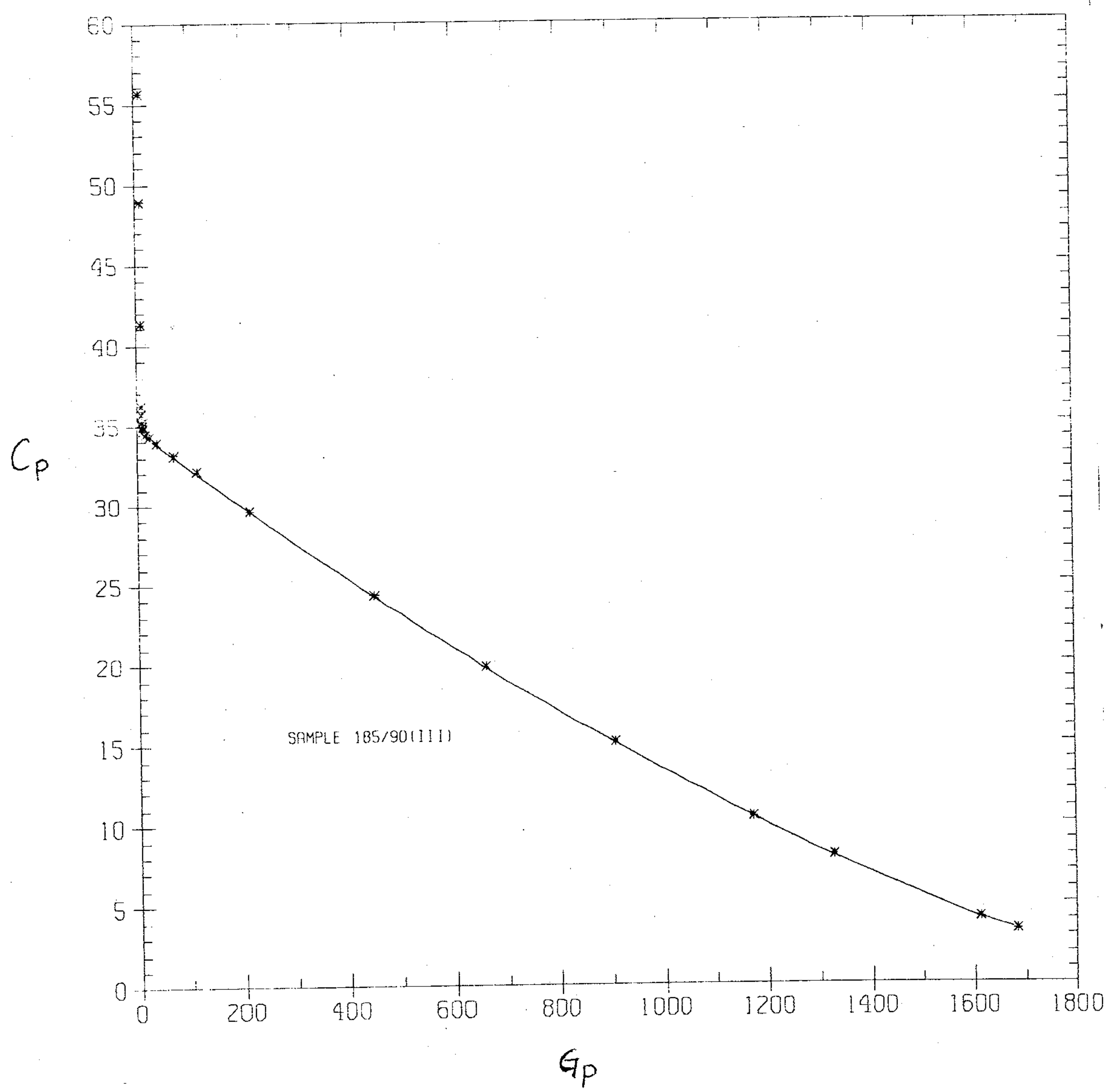


Fig. 7.1(a) Evaluation of dispersion parameters for sample 185/90 at T=-10.2 °C

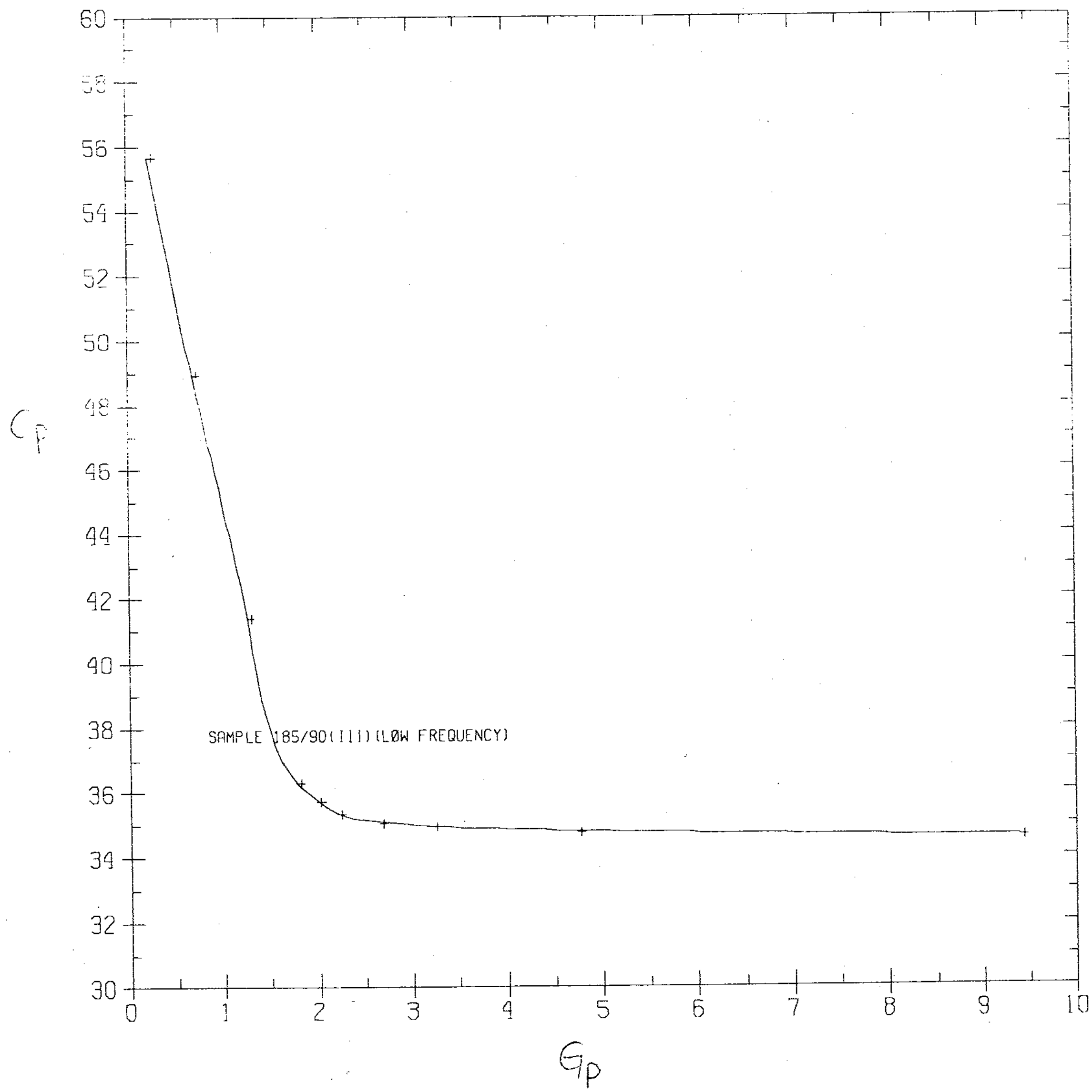


Fig. 7.1(b) Enlarge the low frequencies part of Fig. 7.1(a)

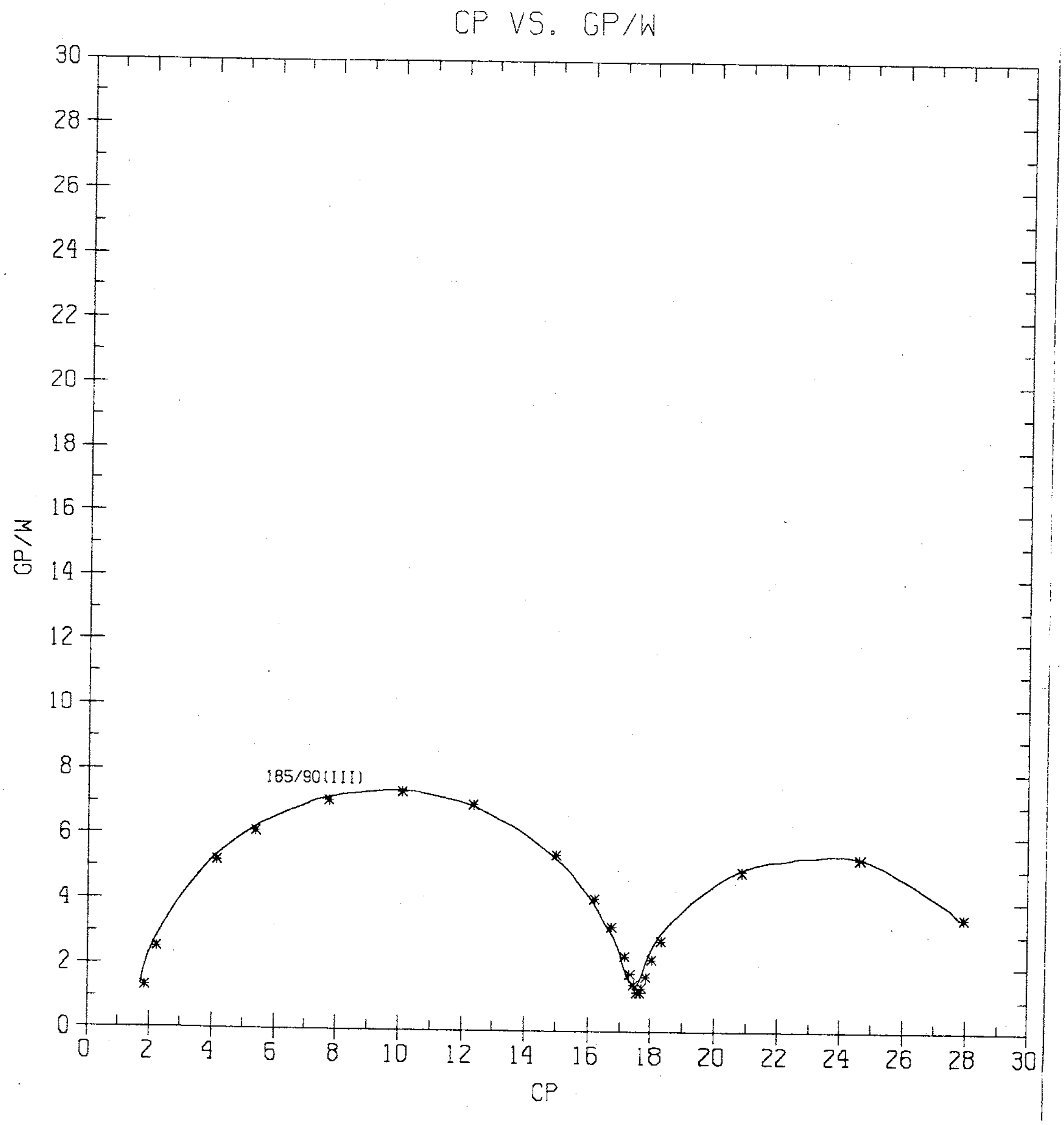


Fig. 7.2(a) Cole-Cole plot for sample 185/90 at T=-10.2 ° C.

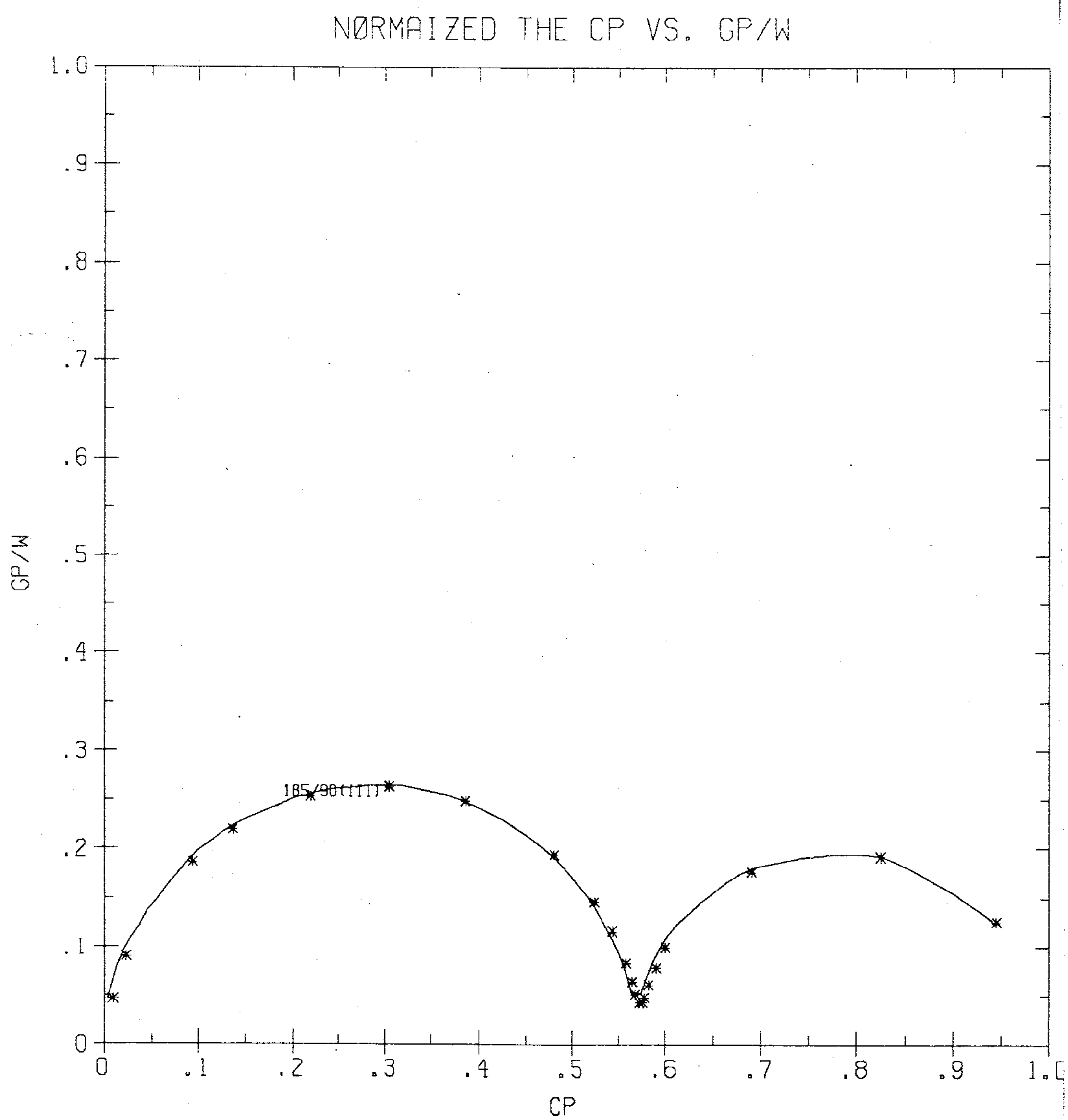


Fig. 7.2(b) Normalized the Cole-Cole plot for sample 185/90 at T=-10.2 ° C (Fig. 7.2(a)).

7.1.2 Results

Our real problems have not been in fitting the p parameters the p-fit procedures are routine but in obtaining good estimates of ϵ_0. Significance loss occurs in calculating p values from X and Y data values, especially at low frequencies. Values of p and of the parameters estimate are highly sensitive to changes of ϵ_0. Expected trends in parameters as temperatures were changed not observed. We have been unable to determine if inconsistencies are caused by measuremental error or by real anomalies between model and data.

The optimal choice of an extrapolation depends on the particular data set. The considerations involved are the accuracy of the data measurements and the difference in the X values of the points used for extrapolation. Measurement errors are amplified in the extrapolation, the amplification increasing with the number of data points used. Low order extrapolation is preferable when measurement error is of the sample range as X differences and high order extrapolation when X differences are relatively large. The ice conductivity parameters f_0 is calculated from q values, a value of f_0 is calculated at each data point and the average value designated f_0.

For the evaluation of all parameters other than ϵ_0 best accuracy estimates is obtained with restricted range of data. About eight data points should be sufficient for good accuracy estimates of parameters, while retaining the ability to detect data anomalies with some experience, it should be possible to rough estimate f from X data and develop a procedure to choose the frequency range before parameters evaluation.

In this study, we checked the bridges with test circuit whose parameters are known, we expect to have reliable measurements and have good accuracy by compare with theoretical data, also inverse theoretical data check the parameters. Using least-squares and point-fitted method computed the parameters the following pages, we will show these fitting results and some sample fitting results. These fitting programs show in Appendix D and E.

7.2 Discussion

7.2.1 Experimental Errors

The errors resulting from voids and electrode polarization are conveniently shown by considering the complex dielectric constant loci found when effects are significant.

Sample Interface the effect is just from an air gap of fractional width in series with the dielectric and condenser plates. This is the reason why we add the "Insulgrease" between them, so decrease this effect.

DC conductance the effect of dc conductance indicated by Cole-Cole plots are not simply an additive one to make the observed loss, expressed by ϵ'', too large, as the apparent values of ϵ' are also too large, the errors in both quantities increasing at low frequencies. That the larger apparent dielectric constants are not real, but rather result from conditions at the electrode-dielectric interface, was established by the fact that they decreased with increasing electrode separation. What might be called the "direct" conductance error, namely the additive contribution to ϵ'' from dc conductance, was corrected for by subtraction of the measured limiting low frequency conductance.

Other errors from the measuremental data and the Cole-Cole plots some times sample inhomogeneity or electrode effects may be happened. I believe that errors resulting from the measurements are small in our results. The accuracy of the data reported in this study is limited primarily by slight uncertainties in the cell constants, measurement and control of temperatures, and frequencies of the bridge oscillator (further work).

Section 8 : Conclusion

Comparing our results, we must say that these results are not dependent of the total thickness of the sample; only the relation between the thickness of the conducting and the insulating layers.

We have made experimentals with pure ice and a different thickness; at the high temperature the two or three ranges of dispersion are very well separated; however, the range linked to conductivity is then at very low frequencies.

At the same sample, and same situation, least-squares method got more better results than point-fitted method. In the point-fitted method, in order to calculate the dispersion parameters, we need to choose four data points. There are several point types, if we chose can get better fitting results and reasonable mathematic model parameters. First, if the points, whose Y values are larger. Second, on Cole-Cole plot the points whose Y values are relative maximum. Third, the points whose frequencies cover F1 or F2. Choosing the above point types, we can get the better fitting parameters.

When we do point-fit or least-squares E_0 evaluation, using four-point extrapolation. If we chose the low frequency data, their difference is very small, we can not get the reasonable value. In this case, we need to truncate some low frequency points, then we can get satisfied fitting results.

Section 9 : Suggestion For Further Work

1. Creates the libraries of programmed subroutines, put the whole subroutines and subprograms in the libraries. It is only necessary to call for the subroutine where needed in your program.
2. Consider the effect of pressure on the dielectric properties of ice. In old sample cell, we knew that using the same sample, and same situation, but in different pressure. we get the different measuremental values.
3. Should be mentioned, in constant strain-rate tests on pure ice.
4. Weight the data, and assume a priori standard deviations for the unknowns (parameters); assume the unknowns are statistically independent. Using inverse technique check the data and parameter values, and compared with our fitting results.

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Appendix A : DIEL

Program DIEL computes parallel capacitance (C_p), parallel conductance (G_p), circular frequency (ω), parallel conductance divided by circular frequency (G_p/ω), dielectric constant ϵ' (eps1), dielectric loss ϵ'' (eps2), conductivity σ (sig), and epsilon double prime multiplied by the circular frequency $\epsilon''\omega$ (eps2w).

This program processes measured data from the GR and LF bridges :

With the GR bridge, measurements are made in terms of either series or parallel components. The choice is a matter of instrumental sensitivity, which is frequency dependent. Precision, accuracy and sensitivity at kHz frequencies and higher are usually better with the series configuration. The series notation is shown in Fig. A.1a, where C_s is pure capacitive component and R_s is the series resistance or loss component. The vector diagram for the series equivalent circuit is given in Fig. A.1b, where θ is the phase angle and δ is the dielectric-loss angle.

In the series equivalent case, the dissipation factor D, defined as the cotangent of the dielectric phase angle, is :

$$D = \cot\theta = \tan\delta = \frac{R_s}{\frac{1}{\omega C_s}} = \omega C_s R_s \ .$$

The parallel notation is shown in Fig. A.1c, where R_p is resistance and represents the loss component, G_p is the conductance, and the capacitance C_p is the pure capacitive component. The vector diagram for the parallel equivalent circuit is shown in Fig. A.1d, where θ is the phase angle and δ is the dielectric-loss angle.

Then, the dissipation factor D is :

$$D = \cot\theta = \tan\delta = \frac{G}{\omega C_p} = \frac{1}{\omega C_p R_p}.$$

The relation of series and parallel equivalent values is :

$$C_p = \frac{C_s}{1+D^2} = \frac{C_s}{1+\tan^2\delta} = C_s\cos^2\delta, \tag{A.1}$$

$$G_p = \frac{D^2}{R_s(1+D^2)} = \frac{D\omega C_s}{1+D^2}. \tag{A.2}$$

The LF bridge only measures in the parallel configuration, C_p is the same as the readings, $G_p = CD/RG$ where CD and RG are readings of the LF Bridge.

By appropriate calculation, all measured values are transformed into Cp and Gp. From these, from the sample's geometric factor A/L, and from the value of the high-frequency limiting capacitance, we can evaluate the dispersion parameters.

The following pages show the flow diagram and list the program.

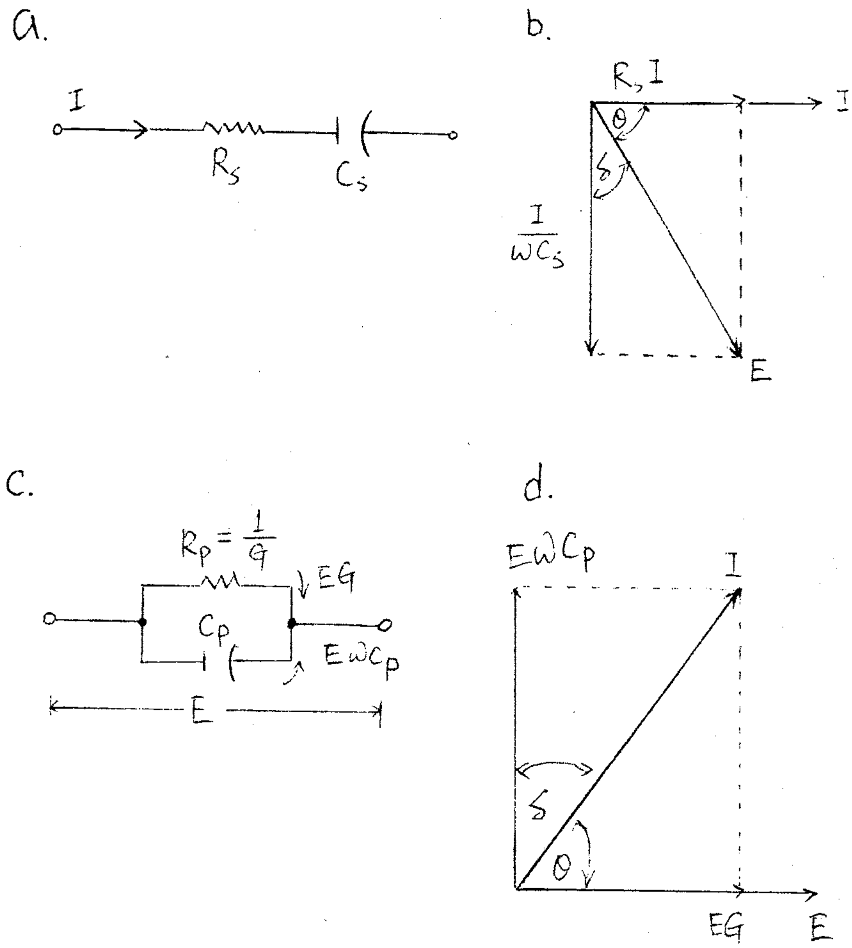
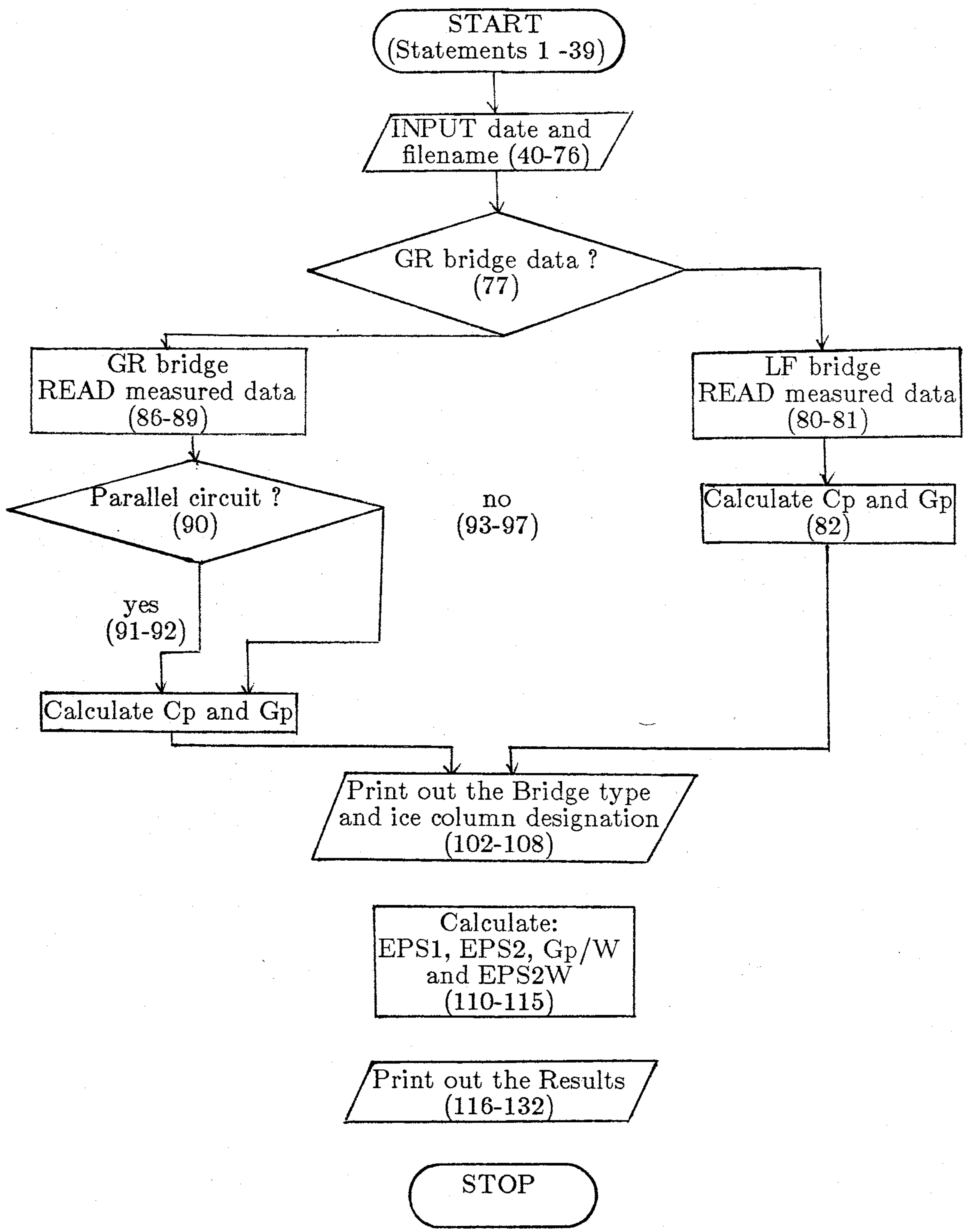


Fig. A.1 Series and parallel equivalent circuits of capacitors.

Flow diagram for DIEL



DIEL program listing

```
c            Program DIEL.FOR
c     al is area/length in cm
c      b = bridge type (l=lf or g=gr bridge)
c     bc = blocking capacitance in pF
c      c = the series or parallel capacitance in pF
c     cd = the counter dial reading from the lf bridge
c     cg = the geometric capacitance
c     cp = the parallel capacitance (measured or calculated) in pF
c      d = the dissipation factor from the GR bridge( if v is the
c           reading from the bridge d = v * the frequency in kHz)
c    dom = date of measurement
c     dp = date of processing
c   eps1 = epsilon'
c   eps2 = epsilon"
c  eps2w = epsilon" * circular frequency
c      f = frequency in kHz
c     gp = the parallel conductance in micro mhos (if gr bridge
c          measurement, be sure that gp is gp * M)
c    gpw = gp / w
c  ifile = input file name
c  ofile = output file name
c     rg = the resistance setting from the lf bridge
c  sigma = conductivity
c     sn = sample number
c      t = type of circuit (1 = parallel, 2 = series)
c  tempc = temperature in degrees centigrade
c  tempk = temperature in degrees Kelvin
c tempin = 1000./temperature in degrees Kelvin
c      v = the dissipation (not yet multiplied by the frequency)
c           or the conductivity * M (from the gr bridge measurements)
c      w = omega, the circular frequency (2*pi*frequency)

        real eps1,eps2,sigma,eps2w,gpw,gp(35),cp(35),cd(35)
        real f(35),w(35),rg(35),v(35),c(35)
        integer t
        character*1 cont
        character*2 b
        character*8 dom,dp
        character*12 ifile,ofile
        character*50 sn
        data pi,eps0/3.14159,8.85e-2/

        write(5,100)
        write(5,110)
        write(5,120)
        write(5,130)
        write(5,140)
100     format(5X,'Hi, before running this program be sure that all')
110     format(5X,'the constants such as blocking capacitance')
120     format(5X,'a/l, and the temperature in degrees C are all')
130     format(5X,'updated for the current sample.  Type c to continue')
```

```
140     format(5X,'or type CTRL d to get out of the program')
        read(5,150)cont
150     format(a)
        write(5,160)
160     format(5X,'enter todays date in the form mo/day/yr')
        read(5,170)dp
170     format(a8)
        write(5,180)
180     format(5X,'enter input file name')
        read(5,190)ifile
190     format(a12)
        write(5,200)
200     format(5X,'enter output file name')
        read(5,190)ofile

        open(UNIT=21,file=ifile,device='dsk',access='seqin')
        l=0
        read(21,210)sn
        read(21,220)dom
210     format(a50)
220     format(a8)
        read(21,230)b
        write(5,230)b
230     format(a2)
        read(21,*)bc,al,tempc
        cg=al*eps0
        write(5,*)al,tempc,cg
        tempk=tempc+273.2
        tempin=1000./tempk

        if(b.eq.'g')goto 250

c...this is the lf bridge portion of the program

        do 240 i=1,35
        read(21,*,end=270)t,f(i),cp(i),cd(i),rg(i)
        write(5,*)t,f(i),cp(i),cd(i),rg(i)
        gp(i)=cd(i)*1.E6/(rg(i)*10000.0)
240     l=l+1
        goto 270

c...this is the gr bridge portion of the program

250     do 260 i=1,35
        read(21,*,end=270)t,f(i),c(i),v(i)
        write(5,280)t,f(i),c(i),v(i)
                w(i)=2.0*pi*f(i)
        if(t.eq.1)then
          cp(i)=c(i)
          gp(i)=v(i)
        else
          d=v(i)*f(i)
          cp(i)=c(i)/(1+d**2)
          gp(i)=w(i)*1.e3*c(i)*1.e-12*d/((1+d**2)*1.e-6)
```

```
          endif
    260   l=l+1
          goto 270

c...this is the main part of the program

    270   open(unit=20,file=ofile,device='dsk',access='seqout')
          if(b.eq.'l') then
            write(20,330)
          else
            write(20,340)
          endif
          write(20,310)dp,sn,dom,cg,al,tempc,tempk,tempin
          write(20,320)
          do 300 i=1,l
          if(t.eq.1) w(i)=2.0*pi*f(i)
          eps1=cp(i)/cg
          eps2=gp(i)/(w(i)*cg*1.e-3)
          sigma=gp(i)/(al*1.e6)
          eps2w=eps2*w(i)
          gpw=(gp(i)/w(i))*1.e3
          write(20,290)cp(i),gpw,gp(i),f(i),w(i),eps1,eps2,sigma,eps2w
    280   format(i2,x,f7.2,3(x,f10.6))
    290   format(9(x,e13.6))
    300   continue
    310   format(1x,'PROCESSING DATE: ',A8,/,'SAMPLE: ',A50,/,'MEASURED ON
          1 ', A8,/,'Teflon foils : o.o1 cm aggregate thickness',/,'Cg = ',F5.2,/,
          2 'AL = ',F5.2,/,'TEMP(C) = ',F7.2,/,'TEMP(K) = ',F8.2,/,
          3 '1000.0/TEMP(K) = ',F6.2 )
    320   format(/,6x,'Cp(pF)',6x,'Gp/w(pF)',6x,'Gp(umhos)',6x,'f(kHz)',
          1 6x,'w(krads/s)',6x,'eps1',11x,'eps2',10x,'sig',11x,'eps2w')
    330   format(35x,'L F  B R I D G E  M E A S U R E M E N T S ')
    340   format(35x,'G R  B R I D G E  M E A S U R E M E N T S')
          close(21)
          close(20)
          stop
          end
```

Input files to DIEL are measurements from the GR and LF bridges. The following format is used for the LF input files :

```
Sample or Model circuit   (Sample name or code)
12/02/86                  (date measured)
l                         (Bridge type)
150.0    10.8 -42.3   (Blocking capacitance, A/L, Temperature in  C)
1    .0001    149.0     0.0  1.e10
1    .0002    148.5     57.2 1.e10
1    .    .    .    .
:    .    .    .    .
:    .    .    .    .
1    .05  146.7     581.0     1.e7
```

where "1" in the first column signifies parallel, the second column is frequency (kHz), the third column is capacitance, the fourth column is the conductance dial reading (CD), and the fifth column is the conductance range (RG).

The following format is used for the GR input files:

```
Sample or Model circuit   (Sample name or code)
12/02/86                  (date measured)
g                         (Bridge type)
150.0 10.8  -42.3  (Blocking capacitance, A/L, Temperature in  C)
1     .05   148.1 .005898
1     .07   148.0 .011350
1     .10   147.5 .022700
1     .     .     .
:     .     .     .
:     .     .     .
2     1.0   145.0 .13900
2     .     .     .
:     .     .     .
:     .     .     .
2     100.0 9.090 .012300
```

where "1" or "2" in the first column signify parallel or series measurements respectively, the second column is frequency (kHz), the third column is the corresponding parallel or series capacitance, and the fourth column is the corresponding conductance (multiplied by M) or dissipation factor (not multiplied by the frequency yet).

The output file from DIEL is in the following format:

B R I D G E T Y P E
PROCESSING DATE: 12/02/1986
SAMPLE :Sample or Model circuit number
MEASURED ON 12/02/1986
BLOCKING CAPACITANCE : (in pF)
Cg = 0.0 (value in pF)
AL = 0.0 (value in cm)
TEMP(C) = -21.30
TEMP(K) = 251.90
1000.0/TEMP(K) = 3.97
Cp(pF) Gp/W (pF) Gp(umhos) f(KHz) w(krads—s^{-1}) eps1 eps2 sig eps2w
R
E
S
U
L
T
S

Using these output data we can do several plots, like Cole-Cole and epsilon prime vs. frequency and epsilon double prime vs. frequency plots. The following pages show the several sample outputs.

L F B R I D G E M E A S U R E M E N T S

PROCESSING DATE: 08/12/86
SAMPLE: Sample 185/90(III)
MEASURED ON 08/11/86
Telflon foils : 0.01 cm aggregate thicknes
Cg = 0.50
AL = 5.65
TEMP(C) = -10.20
TEMP(K) = 263.00
1000.0/TEMP(K) = 3.80

Cp(pF)	Gp/w(pF)	Gp(umhos)	f(kHz)	w(krads/s)	eps1	eps2	sig	eps2w
0.278200E+02	0.354279E+01	0.111300E-03	0.500000E-02	0.314159E-01	0.556766E+02	0.709025E+01	0.197131E-10	0.222747E+00
0.244800E+02	0.539536E+01	0.339000E-03	0.100000E-01	0.628318E-01	0.489922E+02	0.107978E+02	0.600425E-10	0.678446E+00
0.207100E+02	0.497625E+01	0.625333E-03	0.200000E-01	0.125664E+00	0.414473E+02	0.995905E+01	0.110757E-09	0.125149E+01
0.181500E+02	0.281917E+01	0.885667E-03	0.500000E-01	0.314159E+00	0.363239E+02	0.564205E+01	0.156866E-09	0.177250E+01

G R B R I D G E M E A S U R E M E N T S

PROCESSING DATE: 08/12/86
SAMPLE: Sample 185/90 (III)
MEASURED ON 08/11/86
Telflon foils : 0.01 cm aggregate thicknes
Cg = 0.50
AL = 5.65
TEMP(C) = -10.20
TEMP(K) = 263.00
1000.0/TEMP(K) = 3.80

Cp(pF)	Gp/w(pF)	Gp(umhos)	f(kHz)	w(krads/s)	eps1	eps2	sig	eps2w
0.182500E+02	0.286479E+01	0.900000E-03	0.500000E-01	0.314159E+00	0.365240E+02	0.573336E+01	0.159405E-09	0.180119E+01
0.178800E+02	0.225091E+01	0.990000E-03	0.700000E-01	0.439823E+00	0.357835E+02	0.450478E+01	0.175345E-09	0.198130E+01
0.176770E+02	0.175071E+01	0.110000E-02	0.100000E+00	0.628318E+00	0.353773E+02	0.350372E+01	0.194828E-09	0.220145E+01
0.175430E+02	0.140056E+01	0.132000E-02	0.150000E+00	0.942477E+00	0.351091E+02	0.280297E+01	0.233794E-09	0.264174E+01
0.174800E+02	0.127324E+01	0.160000E-02	0.200000E+00	0.125664E+01	0.349830E+02	0.254816E+01	0.283386E-09	0.320211E+01
0.174000E+02	0.125202E+01	0.236000E-02	0.300000E+00	0.188495E+01	0.348229E+02	0.250569E+01	0.417995E-09	0.472311E+01
0.172910E+02	0.149224E+01	0.468800E-02	0.500000E+00	0.314159E+01	0.346048E+02	0.298644E+01	0.830322E-09	0.938217E+01
0.171810E+02	0.184165E+01	0.810000E-02	0.700000E+00	0.439823E+01	0.343846E+02	0.368573E+01	0.143464E-08	0.162107E+02
0.170071E+02	0.237930E+01	0.149496E-01	0.100000E+01	0.628318E+01	0.340367E+02	0.476173E+01	0.264781E-08	0.299188E+02
0.165868E+02	0.329165E+01	0.310230E-01	0.150000E+01	0.942477E+01	0.331954E+02	0.658762E+01	0.549469E-08	0.620868E+02
0.160683E+02	0.411670E+01	0.517319E-01	0.200000E+01	0.125664E+02	0.321578E+02	0.823882E+01	0.916258E-08	0.103532E+03
0.148511E+02	0.547562E+01	0.103213E+00	0.300000E+01	0.188495E+02	0.297218E+02	0.109584E+02	0.182807E-07	0.206562E+03
0.122056E+02	0.699989E+01	0.219908E+00	0.500000E+01	0.314159E+02	0.244272E+02	0.140090E+02	0.389493E-07	0.440105E+03
0.994451E+01	0.740667E+01	0.325762E+00	0.700000E+01	0.439823E+02	0.199021E+02	0.148231E+02	0.576979E-07	0.651953E+03
0.758602E+01	0.712707E+01	0.447806E+00	0.100000E+02	0.628318E+02	0.151820E+02	0.142635E+02	0.793139E-07	0.896203E+03
0.525083E+01	0.616238E+01	0.580790E+00	0.150000E+02	0.942477E+02	0.105086E+02	0.123329E+02	0.102868E-06	0.116234E+04
0.401616E+01	0.523868E+01	0.658312E+00	0.200000E+02	0.125664E+03	0.803761E+01	0.104843E+02	0.116598E-06	0.131749E+04
0.206477E+01	0.254999E+01	0.801101E+00	0.500000E+02	0.314159E+03	0.413225E+01	0.510333E+01	0.141888E-06	0.160326E+04
0.168709E+01	0.133280E+01	0.837422E+00	0.100000E+03	0.628318E+03	0.337640E+01	0.266735E+01	0.148321E-06	0.167595E+04

L F B R I D G E M E A S U R E M E N T S

PROCESSING DATE: 08/24/86
SAMPLE: Sample U185/90 (II)
MEASURED ON 08/23/86
Telflon foils : 0.01 cm aggregate thickness
Cg = 0.65
AL = 7.33
TEMP(C) = -9.90
TEMP(K) = 263.30
1000.0/TEMP(K) = 3.80

Cp(pF)	Gp/w(pF)	Gp(umhos)	f(kHz)	w(krads/s)	eps1	eps2	sig	eps2w
0.327000E+02	0.135918E+01	0.854000E-05	0.100000E-02	0.628318E-02	0.504219E+02	0.209580E+01	0.116539E-11	0.131683E-01
0.318200E+02	0.235788E+01	0.296300E-04	0.200000E-02	0.125664E-01	0.490650E+02	0.363575E+01	0.404340E-11	0.456881E-01
0.299800E+02	0.449454E+01	0.141200E-03	0.500000E-02	0.314159E-01	0.462278E+02	0.693037E+01	0.192686E-10	0.217724E+00
0.270800E+02	0.537414E+01	0.337667E-03	0.100000E-01	0.628318E-01	0.417561E+02	0.828667E+01	0.460790E-10	0.520666E+00
0.236000E+02	0.488871E+01	0.614333E-03	0.200000E-01	0.125664E+00	0.363901E+02	0.753817E+01	0.838337E-10	0.947273E+00
0.211000E+02	0.290299E+01	0.912000E-03	0.500000E-01	0.314159E+00	0.325352E+02	0.447627E+01	0.124454E-09	0.140626E+01

G R B R I D G E M E A S U R E M E N T S

PROCESSING DATE: 08/24/86
SAMPLE: Sample U185/90U II
MEASURED ON 08/23/86
Telflon foils : 0.01 cm aggregate thickness
Cg = 0.65
AL = 7.33
TEMP(C) = -9.90
TEMP(K) = 263.30
1000.0/TEMP(K) = 3.80

Cp(pF)	Gp/w(pF)	Gp(umhos)	f(kHz)	w(krads/s)	eps1	eps2	sig	eps2w
0.211600E+02	0.309079E+01	0.971000E-03	0.500000E-01	0.314159E+00	0.326277E+02	0.476586E+01	0.132505E-09	0.149724E+01
0.207600E+02	0.243280E+01	0.107000E-02	0.700000E-01	0.439823E+00	0.320110E+02	0.375126E+01	0.146015E-09	0.164989E+01
0.204950E+02	0.194169E+01	0.122000E-02	0.100000E+00	0.628318E+00	0.316023E+02	0.299400E+01	0.166485E-09	0.188118E+01
0.203000E+02	0.157033E+01	0.148000E-02	0.150000E+00	0.942477E+00	0.313017E+02	0.242138E+01	0.201965E-09	0.228209E+01
0.202094E+02	0.143240E+01	0.180000E-02	0.200000E+00	0.125664E+01	0.311620E+02	0.220869E+01	0.245633E-09	0.277552E+01
0.200890E+02	0.139526E+01	0.263000E-02	0.300000E+00	0.188495E+01	0.309763E+02	0.215143E+01	0.358897E-09	0.405534E+01
0.199440E+02	0.161192E+01	0.506400E-02	0.500000E+00	0.314159E+01	0.307527E+02	0.248551E+01	0.691048E-09	0.780845E+01
0.198149E+02	0.195442E+01	0.859600E-02	0.700000E+00	0.439823E+01	0.305537E+02	0.301363E+01	0.117303E-08	0.132546E+02
0.196363E+02	0.249381E+01	0.156690E-01	0.100000E+01	0.628318E+01	0.302782E+02	0.384534E+01	0.213824E-08	0.241609E+02
0.192256E+02	0.340871E+01	0.321263E-01	0.150000E+01	0.942477E+01	0.296450E+02	0.525607E+01	0.438404E-08	0.495372E+02
0.187351E+02	0.423413E+01	0.532076E-01	0.200000E+01	0.125664E+02	0.288886E+02	0.652883E+01	0.726086E-08	0.820436E+02
0.175307E+02	0.567995E+01	0.107064E+00	0.300000E+01	0.188495E+02	0.270315E+02	0.875821E+01	0.146103E-07	0.165088E+03
0.149945E+02	0.733231E+01	0.230351E+00	0.500000E+01	0.314159E+02	0.231208E+02	0.113061E+02	0.314344E-07	0.355191E+03
0.126699E+02	0.801485E+01	0.352511E+00	0.700000E+01	0.439823E+02	0.195364E+02	0.123585E+02	0.481047E-07	0.543556E+03
0.999381E+01	0.804002E+01	0.505169E+00	0.100000E+02	0.628318E+02	0.154100E+02	0.123973E+02	0.689368E-07	0.778947E+03
0.723173E+01	0.722450E+01	0.680892E+00	0.150000E+02	0.942477E+02	0.111510E+02	0.111398E+02	0.929165E-07	0.104990E+04
0.565149E+01	0.629802E+01	0.791432E+00	0.200000E+02	0.125664E+03	0.871433E+01	0.971125E+01	0.108001E-06	0.122035E+04
0.304123E+01	0.319177E+01	0.100272E+01	0.500000E+02	0.314159E+03	0.468944E+01	0.492157E+01	0.136835E-06	0.154615E+04
0.249796E+01	0.167863E+01	0.105471E+01	0.100000E+03	0.628318E+03	0.385174E+01	0.258837E+01	0.143929E-06	0.162632E+04

Append B : FITTST and FITPQ

FITTST generates a dielectric spectrum for the equivalent circuit of Fig. B.1. Our fitting parameters are F0, E0, E1, E2, T1, T2, EI, and

$$P = E_I + \frac{E_1}{1+f^2T_1^2} + \frac{E_2}{1+f^2T_2^2} \tag{5.3a}$$

$$Q = \frac{F_0}{f} + \frac{E_1T_1f}{1+f^2T_1^2} + \frac{E_2T_2f}{1+f^2T_2^2}. \tag{5.3b}$$

Using the above equations we compute X, Y by the following equations

$$X = \frac{E_0[(E_0+P)P+Q^2]}{(E_0+P)^2+Q^2} \tag{5.4c}$$

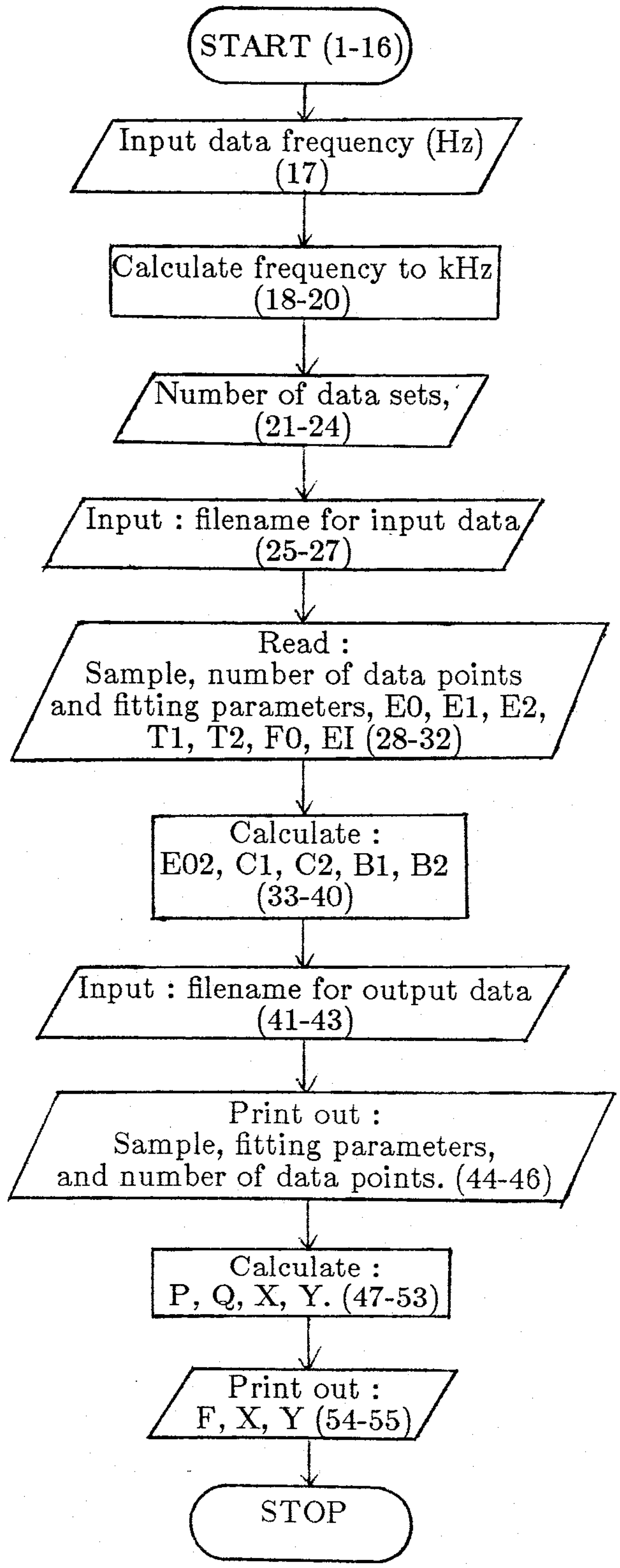
$$Y = \frac{E_0^2Q}{(E_0+P)^2+Q^2}. \tag{5.4d}$$

FITPQ generates a dielectric spectrum for the equivalent circuit of Fig. B.1 minus the blocking capacitor (E_0). The listing for this program is shown on a subsequent page.

Synthetic spectra are used for model analysis and program checks (See App. D).

The following pages show the flow diagram for these programs, the program listings, and one example each for input and output.

Flow diagram for FITTST



FITTST program listing

```
C     FITTST PROGRAM
C     This program calculates the complex relaxation spectrum of ice
C     sandwiched between blocking layers, as a function of dielectric
C     parameters and dc conductance.
C     DESCR : Sample name or code
C     NAME  : Input file name
C     NEW   : Output file name
C     F     : Frequency (hertz)
C     NSETS : Number of data sets
C     NDATA : Number of data
C     Input parameters should be scaled to A1 or A2,
C     as discussed in section 5.3.
C     Input parameters : E0, E1, E2, T1, T2, F0, EI

      CHARACTER*30 DESCR
      CHARACTER*11 NAME,NEW
      DIMENSION F(28)
      DATA F/0.1,0.2,0.5,1.,2.,5.,7.,10.,20.0,50.,70.,100.,150.,200.
     1,300.,500.,700.,1000., 1500.,2000.,3000.,5000.,7000.,10000.
     1, 15000.,20000.,50000., 100000./

      DO 100 I=1,28
      F(I)=F(I)/1000.
  100 CONTINUE

C     READ IN THE NUMBER OF DATA SETS

      WRITE(5,*)' INPUT NUMBER OF DATA SETS '
      READ(5,*)NSETS

      DO 300 I= 1,NSETS

      WRITE(5,*)' INPUT FILE NAME '
      READ(5,110)NAME
      OPEN(UNIT=21,DEVICE='DSK',FILE=NAME)
      READ(21,110)DESCR
      READ(21,120)NDATA
      READ(21,130)E0,E1,E2,T1,T2,F0,EI
C     READ(21,130)E0,E1,E2,TAU1,TAU2,SIGMA0,EI
      CLOSE(UNIT=21)

      E02=E0**2
C     F0=SIGMA0/1000./2/3.14159/8.85E-14
C     T1=TAU1*1000.*2*3.14159
C     T2=TAU2*1000.*2*3.14159
      C1=T1**2
      C2=T2**2
      B1=E1*T1
      B2=E2*T2
      WRITE(5,*)'INPUT NEW FILE NAME '
      READ(5,110)NEW
```

```
0043          OPEN(UNIT=22,DEVICE='DSK',FILE=NEW)
0044          WRITE(22,110)DESCR
0045          WRITE(22,140)E0,E1,E2,T1,T2,F0,EI
0046          WRITE(22,150)NDATA
0047          DO 200 J=1,NDATA
0048          FF=F(J)**2
0049          P=EI + E2/(1+C2*FF) + E1/(1+C1*FF)
0050          SQ=F0+(B2/(1+C2*FF)+B1/(1+C1*FF))*FF
0051          Q=SQ/F(J)
0052          X=E0*((E0+P)*P+Q**2)/((E0+P)**2+Q**2)
0053          Y=E02*Q/((E0+P)**2+Q**2)
0054          WRITE(22,160)F(J),X,Y
0055    200   CONTINUE
0056          CLOSE(UNIT=22)
0057    300   CONTINUE
0058    110   FORMAT(A)
0059    120   FORMAT(I)
0060    130   FORMAT(7F)
0061    140   FORMAT(1X,7(F9.5,1X))
0062    150   FORMAT(1X,I2)
0063    160   FORMAT(3F)
0064          STOP
0065          END
```

Note : 30/31 and 34-36 are alternative statements for scaling purposes, if input was not properly scaled.

INPUT DATA

Test data (row 1)
28 (row 2)
100.0 100.0 5.0 1.0 0.20 100.0 0.0 (row 3)

row 1 : Name of data (Test data, Model circuit or sample number).

row 2 : Number of data points.

row 3 : Fitting parameters, E0, E1, E2, T1, T2, F0, EI.

OUTPUT DATA

Test data (row 1)
100.00000 100.00000 5.00000 1.00000 0.20000 100.00000 0.00000 (row 2)
28 (row 3)

row 1 : Name of data (Test data, Model circuit, or Sample number).

row 2 : Fitting parameters, E0, E1, E2, T1, T2, F0, EI.

row 3 : Number of data points.

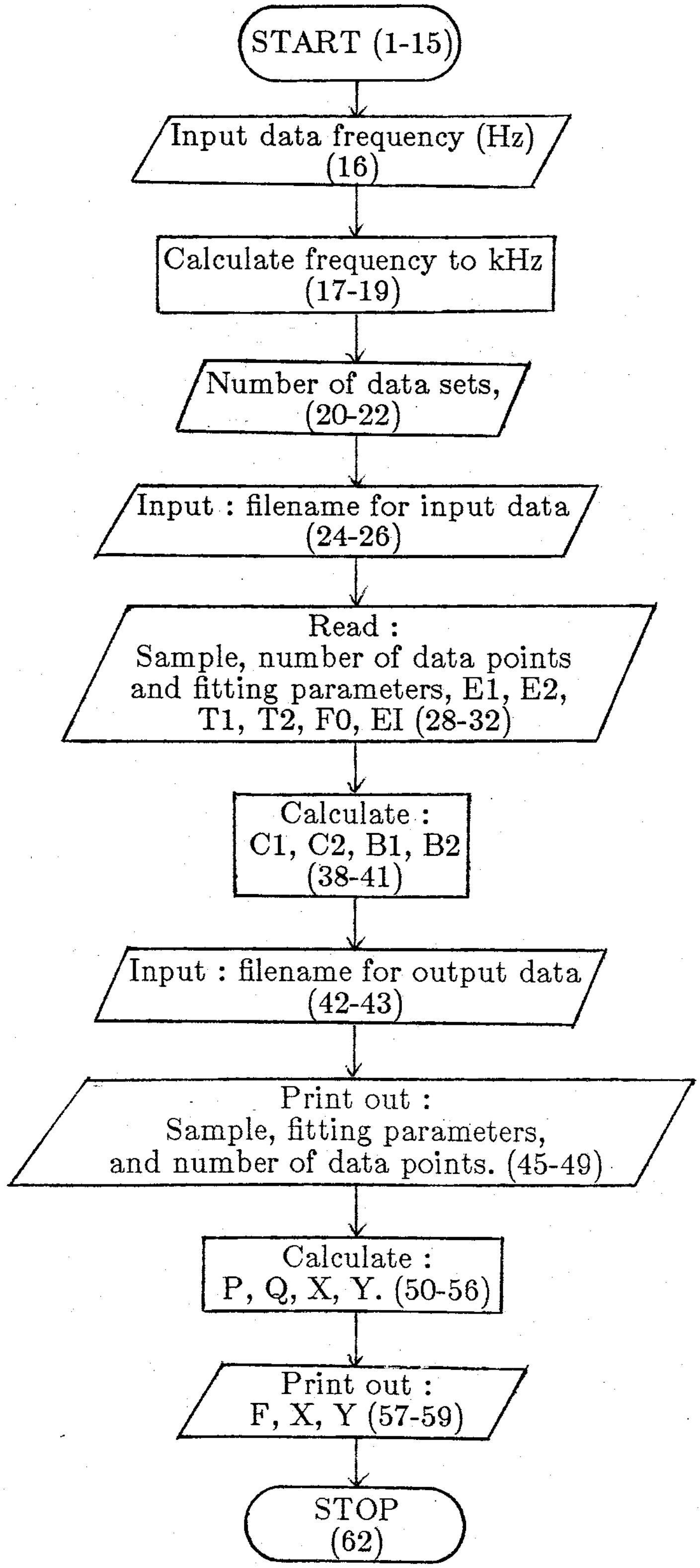
0.0001000	99.9999990	0.0100000
0.0002000	99.9999914	0.0200000
0.0005000	99.9999495	0.0499999
0.0010000	99.9997950	0.0999995
0.0020000	99.9991808	0.1999958
0.0050000	99.9948759	0.4999349
0.0070000	99.9899588	0.6998213
0.0100000	99.9795141	0.9994791
0.0200000	99.9182196	1.9958417
0.0500000	99.4959497	4.9359653
0.0700000	99.0274305	6.8271444
0.1000000	98.0785179	9.5128645
0.1500000	95.9886227	13.4801103
0.2000000	93.5170212	16.7413669
0.3000000	88.3686705	21.3532152
0.5000000	79.9064159	26.1281128
0.7000000	73.8929234	28.9156563
1.0000000	66.8894596	32.2879176
1.5000000	56.8409538	36.4121637
2.0000000	47.9140329	38.4323640
3.0000000	33.9770818	38.0649605
5.0000000	18.5146980	31.9752445
7.0000000	11.3078239	26.2174544
10.0000000	6.2731737	20.1265647
15.0000000	3.0195364	14.2227808
20.0000000	1.7518687	10.9091325
50.0000000	0.2904451	4.4771899
100.0000000	0.0729956	2.2471299

First column : Frequency (kHz).

Second column : X

Third column : Y

Flow diagram for FITPQ



FITPQ program listing

```
C    PROGRAM FITPQ.FOR
C    This program calculates the complex relaxation spectrum of ice
C    without blocking layers.
C    DESCR : Sample name or code
C    NAME  : Input file name
C    NEW   : Output file name
C    F     : Frequency (hertz)
C    NSETS : Number of data sets
C    NDATA : Number of data
C    Input parameters shlould be scaled to A1 or A2,
C    as discussed in section 5.3
C    Input parameters : E1,E2,T1,T2,F0,EI

     CHARACTER*30 DESCR
     CHARACTER*11 NAME,NEW
     DIMENSION F(28)
     DATA F/0.1,0.2,0.5,1.,2.,5.,7.,10.,20.0,50.,70.,100.,150.,200.
     1,300.,500.,700.,1000., 1500.,2000.,3000.,5000.,7000.,10000.
     1, 15000.,20000.,50000., 100000./

     DO 200 I=1,28
     F(I)=F(I)/1000.
200  CONTINUE

C    READ IN THE NUMBER OF DATA SETS

     WRITE(5,*)' INPUT NUMBER OF DATA SETS '
     READ(5,*)NSETS

     DO 400 I= 1,NSETS

     WRITE(5,*)' INPUT FILE NAME '
     READ(5,210)NAME
210  FORMAT(A)

     OPEN(UNIT=21,DEVICE='DSK',FILE=NAME)

     READ(21,210)DESCR
     READ(21,220)NDATA
220  FORMAT(I)
     READ(21,230)E1,E2,T1,T2,F0,EI
230  FORMAT(6F)
C    READ(21,230)E1,E2,TAU1,TAU2,SIGMA0,EI

     CLOSE(UNIT=21)

C    F0=SIGMA0/1000./2/3.14159/8.85E-14
C    T1=TAU1*1000.*2*3.14159
C    T2=TAU2*1000.*2*3.14159
     C1=T1**2
     C2=T2**2
```

```
0040       B1=E1*T1
0041       B2=E2*T2
0042       WRITE(5,*)'input new file name '
0043       READ(5,210)NEW
0044       OPEN(UNIT=22,DEVICE='DSK',FILE=NEW)
0045       WRITE(22,210)DESCR
0046       WRITE(22,240)E1,E2,T1,T2,F0,EI
0047  240  FORMAT(1X,6(F9.5,1X))
0048       WRITE(22,250)NDATA
0049  250  FORMAT(1X,I2)
0050       DO 300 J=1,NDATA
0051       FF=F(J)**2
0052       P=EI + E2/(1+C2*FF) + E1/(1+C1*FF)
0053       SQ=F0+(B2/(1+C2*FF)+B1/(1+C1*FF))*FF
0054       Q=SQ/F(J)
0055       X=P
0056       Y=Q
0057       WRITE(22,260)F(J),X,Y
0058  260  FORMAT(3F)
0059  300  CONTINUE

0060       CLOSE (UNIT=22)

0061  400  CONTINUE
0062       STOP
0063       END
```

Note : 31/33 and 35-37 are alternative statements for scaling purposes, if input was not properly scaled.

INPUT DATA

TEST FITPQ DATA (row 1)
28 (row 2)
78.45000 0.00000 0.18220 0.00000 75.91000 3.12000 (row 3)

row 1 : Name of data (Test data, Model circuit or ssample number).

row 2 : Number of data points.

row 3 : Fitting parameters, E1, E2, T1, T2, F0, EI

OUTPUT DATA

TEST FITPQ DATA (row 1)
78.45000 0.00000 0.18220 0.00000 75.91000 3.12000 (row 2)
28 (row 3)

row 1 : Name of data (Test data, Model circuit, or Sample number).

row 2 : Fitting parameters, E1, E2, T1, T2, F0, EI.

row 3 : Number of data points.

0.0001000	81.5699997	759100.0000000
0.0002000	81.5699997	379550.0078125
0.0005000	81.5699987	151820.0058594
0.0010000	81.5699978	75910.0136719
0.0020000	81.5699892	37955.0283203
0.0050000	81.5699339	15182.0715332
0.0070000	81.5698719	10844.3857422
0.0100000	81.5697393	7591.1429443
0.0200000	81.5689583	3795.7858582
0.0500000	81.5634890	1518.9146271
0.0700000	81.5572414	1085.4289551
0.1000000	81.5439653	760.5288849
0.1500000	81.5114460	508.2090988
0.2000000	81.4659662	382.4049301
0.3000000	81.3363123	257.3086357
0.5000000	80.9242849	158.9079704
0.7000000	80.3143225	118.2882204
1.0000000	79.0493841	89.7443333
1.5000000	76.1175985	70.5569105
2.0000000	72.3739500	63.1911397
3.0000000	63.5232320	58.3197403
5.0000000	45.9907026	54.2372108
7.0000000	32.9869957	48.9366517
10.0000000	21.2810507	40.6804342
15.0000000	12.3828790	30.3761148
20.0000000	8.6141838	23.8163056
50.0000000	4.0540164	10.0270896
100.0000000	3.3556080	5.0518767

First column : Frequency (kHz).

Second column : X

Third column : Y

Appendix C : Subroutines

Subroutines and their functions are summarized in Table V. For each of the subroutines we present an analysis, flow diagram, and listing.

C1. Subroutine CALRSD

This subroutine calculates residuals for X, Y, p, and q. X, Y are measured data (supplied by DIEL - see Appendix A), p and q are computed from the measurements or from the dispersion parameters, respectively.

The following equations are used

$$p = E_\infty + \frac{E_1}{1+f^2T_1^2} + \frac{E_2}{1+f^2T_2^2}; \qquad (5.3a)$$

$$q = \frac{F_0}{f} + \frac{E_1 f T_1}{1+f^2T_1^2} + \frac{E_2 f T_2}{1+f^2T_2^2}; \qquad (5.3b)$$

$$p = \frac{E_0[(E_0-X)X-Y^2]}{(E_0-X)^2+Y^2}; \qquad (5.4a)$$

$$q = \frac{E_0^2 Y}{(E_0-X)^2+Y^2}; \qquad (5.4b)$$

$$X = \frac{E_0[(E_0+p)p+q^2]}{(E_0+p)^2+q^2}; \qquad (5.4c)$$

$$Y = \frac{E_0^2 q}{(E_0+p)^2+q^2}. \qquad (5.4d)$$

With E, T values derived previously (subroutine PAR or Point Fit) the "Calculated" values p, q are computed by Eqs. (5.3a, b). Next, substituting "Calculated" p, q into Eqs. (5.4c, d) the "Calculated" X, Y are obtained. Using calculated data X, Y and measured data XD, YD, the subroutine then computes residuals, percent differences, root mean squares for XY, and their average error.

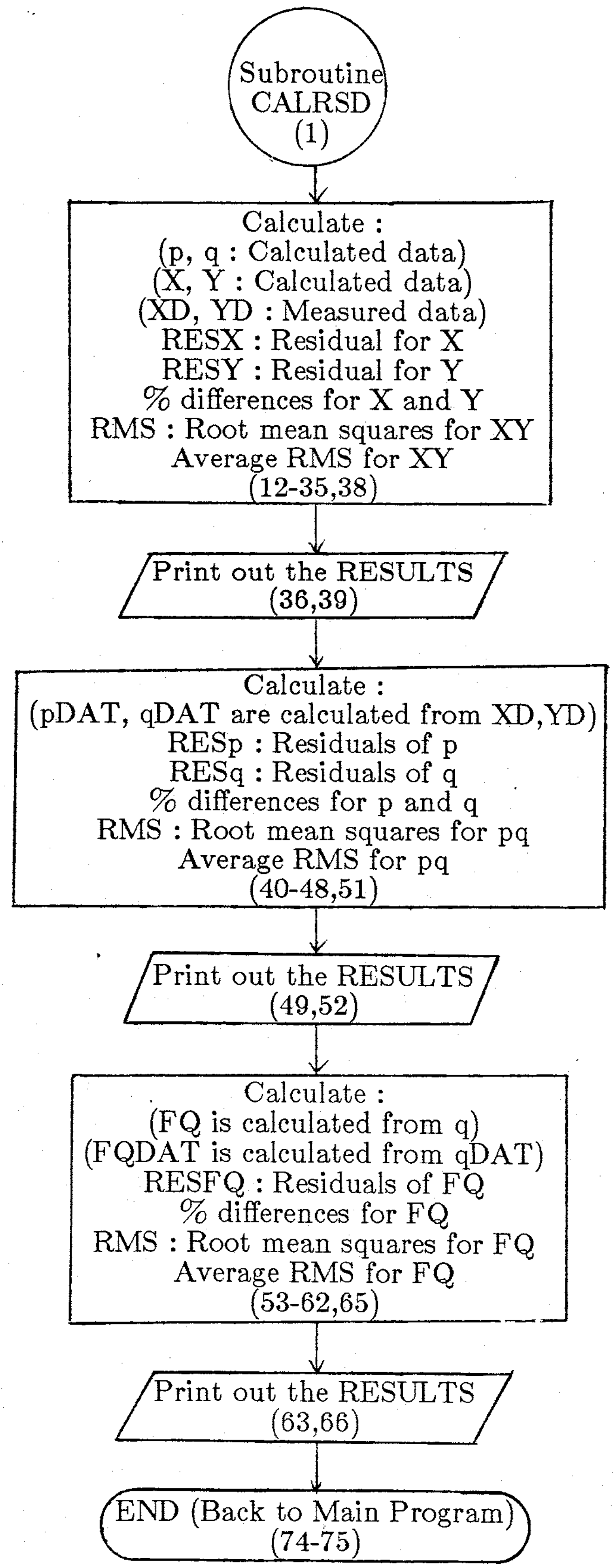
Substituting measured data XD, YD into Eqs. (5.4a, b), we get "Measured" data pDAT, qDAT. Using "Measured" data pDAT, qDAT, and "Calculated" data p, q, we compute the residuals, percent differences, root mean squares for pq, and their average error.

Multiplying Eqs. (5.3b, 5.4b) with f (frequency) "Calculated" and "Measured" fq values, respectively, are obtained. Using these two values, we can compute the residuals, percent differences, and their average error.

According to the above calculated items, we can judge the fitted model. If the values are within a pre-established tolerance, the fitted model is satisfied; otherwise, we need to try again using different frequencies and starting fitting point.

The following pages show the flow diagram and list the subroutine.

Flow diagram for subroutine CALRSD



CALRSD subroutine listing

```
C     CALRSD subroutine
C     Computes residuals between fitted and measured values,
C     respectively of X, Y, P, Q, and fq, rms deviations of
C     XY and FQ

      SUBROUTINE CALRSD
      COMMON /A/NDAT,II,FD(30),XD(30),YD(30),SND,SF2,SF4,MM
      COMMON /C/E0,E02,EI,E1,T1,B1,C1,E2,T2,B2,C2,F0,SR,F1,F2
      DIMENSION PPP(30),QQQ(30),PDAT(30),QDAT(30)

      SUMXY = 0.0
      SUMPQ = 0.0
      SUMFQ = 0.0
      WRITE(3,400)
      DO 430 J = 1,NDAT
      FF = FD(J)*FD(J)
      P = EI + E2 / (1 +  C2 * FF) + E1 / (1 + C1 * FF)
      SQ = F0 + ( B2/(1 + C2 * FF) + B1/(1 + C1 * FF))* FF
      Q = SQ / FD(J)
      PPP(J) = P
      QQQ(J) = Q
      QQ = Q**2
      EP = E0 + P
      D = EP**2 + QQ
      XXX = E0 * ( EP * P + QQ) / D
      YYY = E02 * Q / D
      RESX = XXX - XD(J)
      RESY = YYY - YD(J)
      DIFX = RESX/XXX*100.0
      DIFY = RESY/YYY*100.0
      XRMS = SQRT(( RESX**2 + RESY**2) / (XXX**2 + YYY**2))*100.0
      YY = YD(J)**2
      EXSQ = (E0 - XD(J))**2
      PDAT(J) = E0 * (( E0 - XD(J)) * XD(J) - YY)
     &      /(EXSQ + YY)
      QDAT(J) = E02 * YD(J) / (EXSQ +  YY)
      IF(J.LT.II) GO TO 410

      SUMXY = SUMXY + ABS(XRMS)
  410 WRITE(3,420)FD(J),XD(J),YD(J),XXX,YYY,RESX,RESY,DIFX,DIFY,XRMS
  430 CONTINUE
      XYAVE = SUMXY / SND
      WRITE(3,440)XYAVE

      WRITE(3,450)
      DO 470 J = 1,NDAT
      RESP = PPP(J) - PDAT(J)
      RESQ = QQQ(J) - QDAT(J)
      DIFP = RESP/PPP(J)*100.0
      DIFQ = RESQ/QQQ(J)*100.0
      PRMS = SQRT(( RESP**2 + RESQ**2)/( PDAT(J)**2 + QDAT(J)**2))*100.0
```

```
      IF(J.LT.II) GO TO 460

      SUMPQ = SUMPQ + ABS(PRMS)
 460  WRITE(3,420)FD(J),PDAT(J),QDAT(J),PPP(J),QQQ(J),RESP,RESQ,DIFP,
      1 DIFQ,PRMS
 470  CONTINUE

      PQAVE = SUMPQ / SND
      WRITE(3,440)PQAVE

      WRITE(3,480)
      DO 510 J = 1,NDAT
      FF = FD(J)*FD(J)
      FQDAT = FD(J) * QDAT(J)
      DIF = FQDAT - ( B1/(1. + C1 * FF ) + B2/(1. + C2 * FF)) * FF
      FQ = FD(J) * QQQ(J)
      RESFQ = FQ - FQDAT
      FQRMS = RESFQ / FQDAT*100.0

      IF(J.LT.II) GO TO 490
      SUMFQ = SUMFQ + ABS(FQRMS)

 490  WRITE(3,500)FD(J),FQDAT,FQ,RESFQ,FQRMS,DIF
 510  CONTINUE
      FQAVE = SUMFQ / SND
      WRITE(3,520)FQAVE

 400  FORMAT(//,T21,'MEASURED',T40,'CALCULATED',T60,'RESIDUALS',T79,
      1 '% DIFFERENCE',T97,'RMSXY',/T21,'--------',T39,'----------'
      1 ,T60,'---------',T79,'------------',T97,'-----',/1X,
      1 'FREQ. (K HZ)',T19,'X',T28,'Y',T39,'X',T49,'Y',T58,'X',T68,
      1 'Y',T78,'X',T88,'Y')
 420  FORMAT(1X,F10.4,4F10.2,5F10.2)
 440  FORMAT(/T92,F10.3//)
 450  FORMAT('1',/,1X,'PAGE : 2 ',//,T21,'MEASURED',T40,'CALCULATED',
      1 T60,'RESIDUALS',T79,'% DIFFERENCE',T97,'RMSPQ',/T21,'--------',
      1 T39,'----------',T60,'---------',T79,'------------',T97,'-----',
      1 /1X,'FREQ. (K HZ)',T19,'P',T28,'Q',T39,'P',T49,'Q',T58,'P',T68,
      1 'Q',T78,'P',T88,'Q')
 480  FORMAT(//,T21,'MEASURED',T39,'CALCULATED',T60,'RESIDUALS',T79,
      1 '% DIFFERENCE',T97,'F0',/T21,'--------',T39,'----------'
      1 ,T60,'---------',T79,'------------',T97,'--',/1X,
      1 'FREQ. (K HZ)',T23,'FQ',T43,'FQ',T63,'FQ',T83,'FQ')
 500  FORMAT(1X,F10.4,5X,F10.3,10X,F10.3,10X,F10.3,10X,F10.3,5X,F10.3)
 520  FORMAT(/T77,F10.3//)
      RETURN
      END
```

C2. Subroutine F0F

This subprogram evaluates F0. X, Y are measured data and E_0 is obtained from the above, so we can get Q by

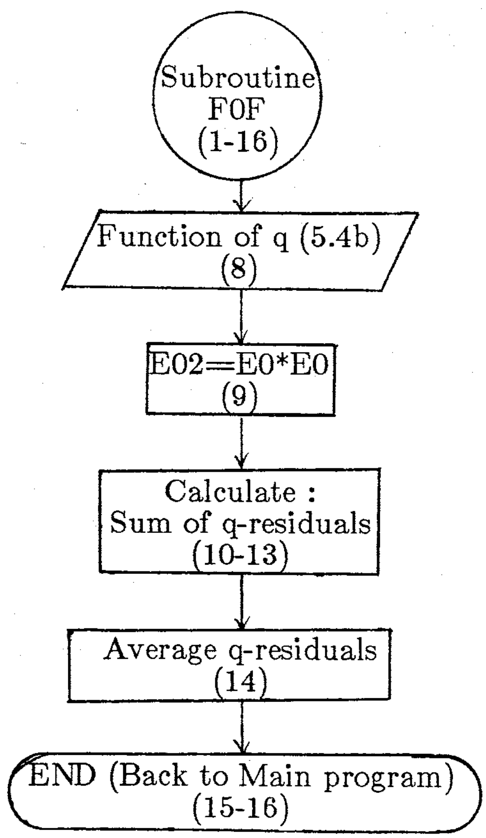
$$Q = \frac{E_0^2 Y}{[(E_0 - X)^2 + Y^2]} \tag{C.1}$$

Our fitting parameters E1, T1, E2, T2 are calculated from subroutine PAR. So we know the following equation

$$Q = \frac{F0}{f} + \frac{E_1 T_1 f}{1 + T_1^2 f^2} + \frac{E_2 T_2 f}{1 + T_2^2 f^2}. \tag{C.2}$$

Set Eq. (C.1) equal to Eq. (C.2), find F0. The following show the flow diagram and list the subroutine.

Flow diagram for subroutine F0F



F0F program listing

```
C     F0F subroutine
C     Computes the dc conductance parameter from the
C     computed q-values at each frequency,
C     then averages them for display as one value.

      SUBROUTINE F0F
      COMMON /A/NDAT,II,FD(30),XD(30),YD(30),SND,SF2,SF4,MM
      COMMON /C/E0,E02,EI,E1,T1,B1,C1,E2,T2,B2,C2,F0,SR,K,D
      FQF(F,X,Y)=E02*F*Y/((E0-X)**2+Y**2)

      E02 = E0**2
      S = 0.
      DO 300 I = II,NDAT,MM
      F = FD(I);      FF = F**2
300   S = S + FQF(F,XD(I),YD(I))
      &      - (B1/(1. + C1*FF) + B2/(1. + C2*FF))*FF
      F0 = S/SND
      RETURN
      END
```

C3. Subroutine MIN

Computes value of E_0 that minimizes the sum of squared deviations.

First step : initiation

Choose two neighboring data points : (XD(1), XD(2)), XD(1) > XD(2).

Let X_2=XD(1)=E_0 and calculate spectrum (subroutine PAR); calculate the sum of residuals S_2 = SR.

Second step : establish a unit E_0 increment

Compute :

$$D = X_2 - XD(2) \ ,$$

if this value is greater than 1,

or

D=1 if the above expression is smaller than 1.

Let $X_1 = X_2 - D = E_0$ and calculate spectrum (subroutine PAR); calculate the sum of squared residuals S_1 = SR.

Third step : determine the direction where the minimum will be found

a. $S_2 > S_1$: this means minimum of squared residuals must lie to left of X_2, then define :

$$X_1 - D = X_3 = E_0.$$

b. $S_1 > S_2$: this means that the minimum of squared residuals must lie to the right of X_1, then define :

$$X_3 = X_2 + D = E_0.$$

Fourth step : interpolation

At this point we have obtained three sums of squared residuals corresponding to three assumed values of E_0 (i.e. X_1, X_2, X_3). The relations are

$$X_2 > X_1 \qquad X_3 > X_1 \quad \text{or} \quad X_3 < X_2$$

$$S_1 < S_2 > S_3.$$

We now interpolate between these values in order to zero in on the minimum and the best of E_0. As shown on the flow diagram, there are six interpolation possibilities depending on the relative magnitudes of S_1, S_2, S_3.

Fifth step : refine the minimum

Calculate the deviation : Let

$$Z_1 = X_1 - X_3 \; ; \; Z_2 = X_2 - X_3$$

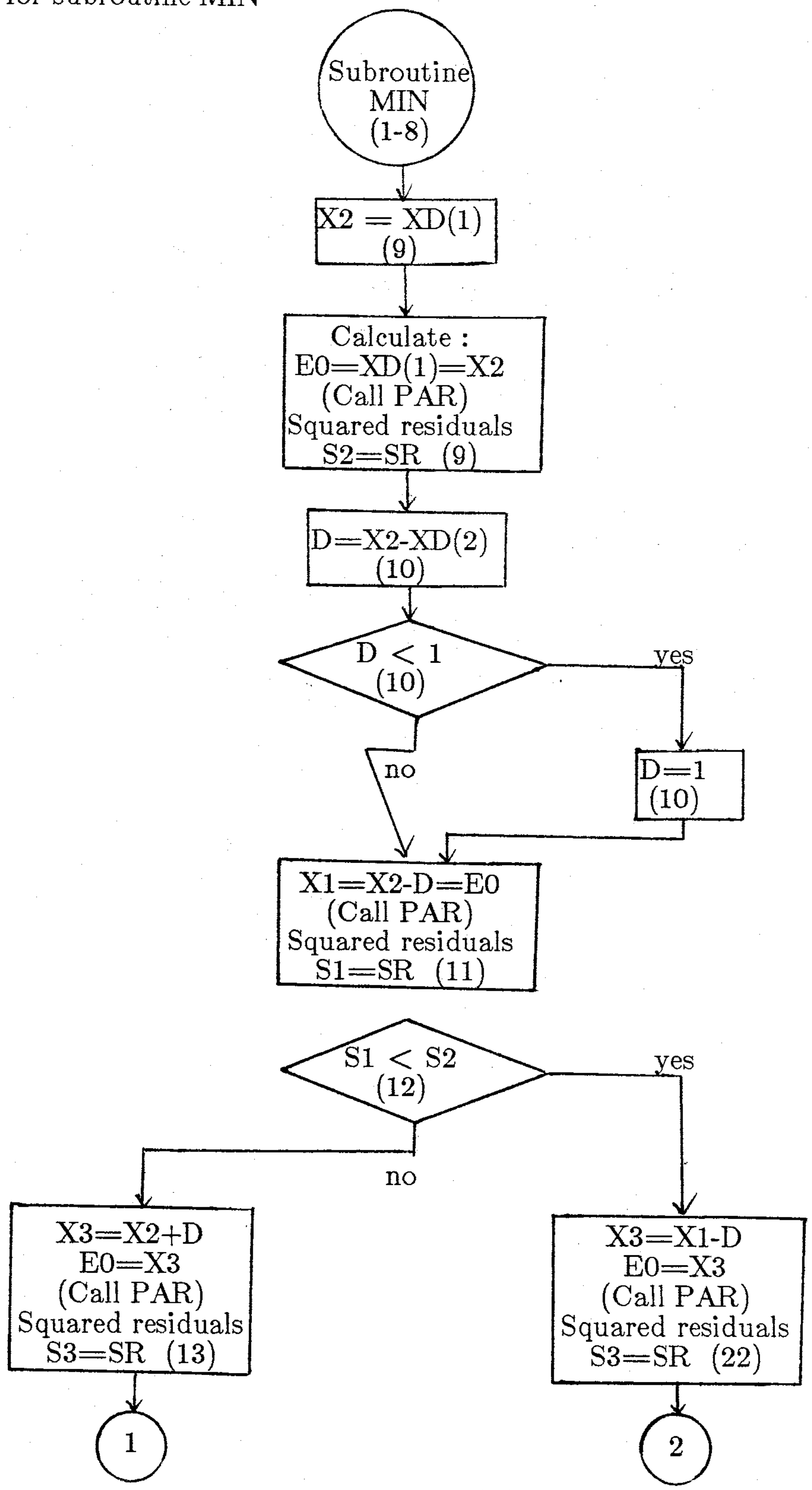
$$Q_1 = (S_1 - S_3)/Z_1 \; ; \; Q_2 = (S_2 - S_3)/Z_2$$

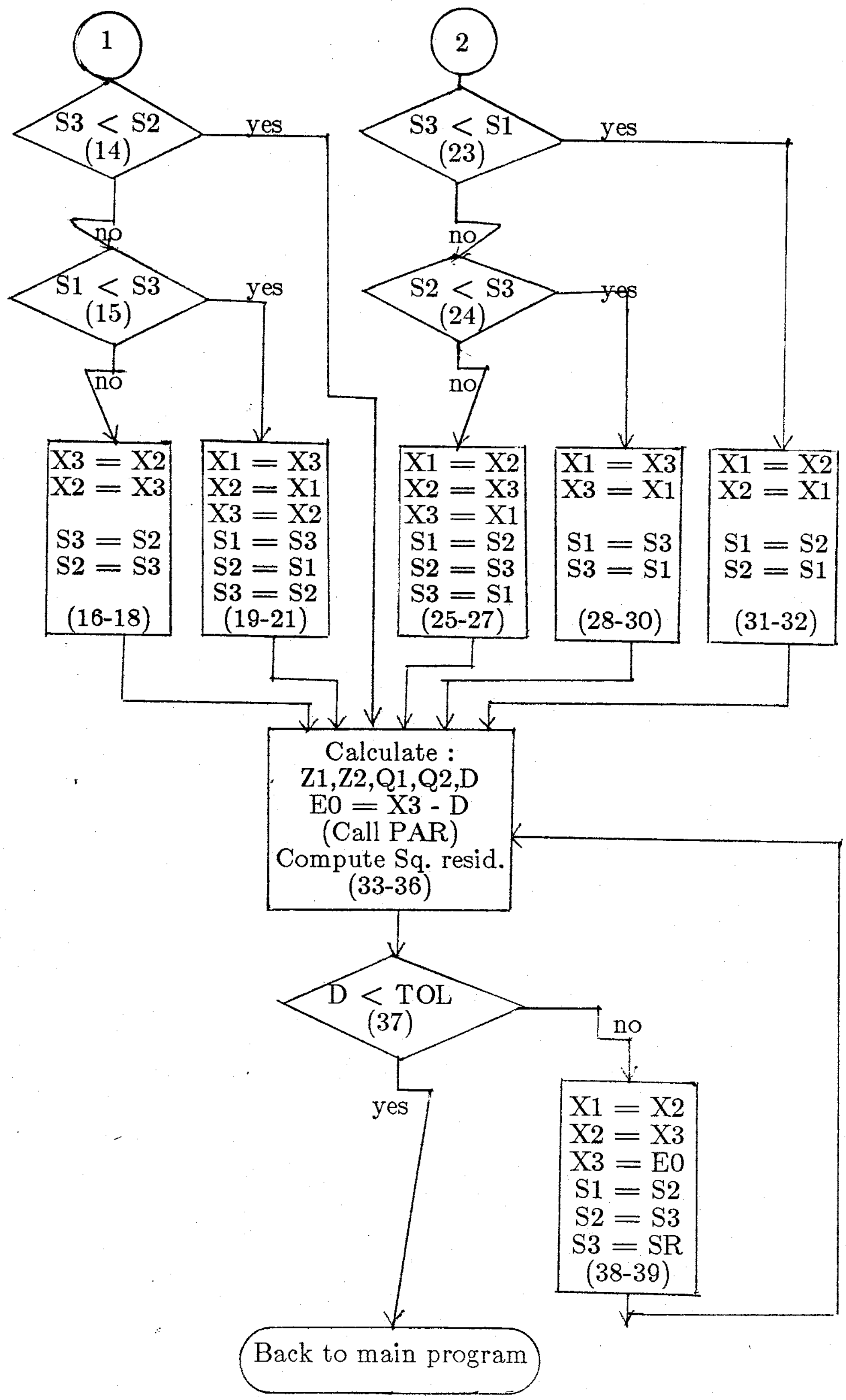
$$D = (Z_2 \times Q_1 - Z_1 \times Q_2)/(Q_2 - Q_1) \times 0.5 \; .$$

Let $E_0 = X_3 - D$. Calculate spectrum and deviation. If the deviation is within a pre-established tolerance, the E_0 is satisfied; otherwise, we need to replace X_1 by X_2, X_2 by X_3, X_3 by E_0, S_1 by S_2, S_2 by S_3, S_3 by SR, and repeat the calculation.

The following pages show the flow diagram and list the subroutine.

Flow diagram for subroutine MIN




1
2
S3 < S2 (14)
yes
no
S1 < S3 (15)
yes
no
S3 < S1 (23)
yes
no
S2 < S3 (24)
yes
no
X3 = X2
X2 = X3
S3 = S2
S2 = S3
(16-18)
X1 = X3
X2 = X1
X3 = X2
S1 = S3
S2 = S1
S3 = S2
(19-21)
X1 = X2
X2 = X3
X3 = X1
S1 = S2
S2 = S3
S3 = S1
(25-27)
X1 = X3
X3 = X1
S1 = S3
S3 = S1
(28-30)
X1 = X2
X2 = X1
S1 = S2
S2 = S1
(31-32)
Calculate :
Z1,Z2,Q1,Q2,D
E0 = X3 - D
(Call PAR)
Compute Sq. resid.
(33-36)
D < TOL (37)
no
yes
X1 = X2
X2 = X3
X3 = E0
S1 = S2
S2 = S3
S3 = SR
(38-39)
Back to main program

MIN subroutine listing

```
C      MIN subroutine
C      This subroutine computes an E0 value by minimiing the sums of
C      deviations between measured X, Y values and those derived with E0
C      values deviating systematically from an initially assumed value.

       SUBROUTINE MIN
       COMMON /A/NDAT,II,FD(30),XD(30),YD(30),SND,SF2,SF4,MM
       COMMON /C/E0,E02,EI,E1,T1,B1,C1,E2,T2,B2,C2,F0,SR,K,D,F1,F2

       K=0

       X2=XD(1)   ;  E0=X2     ; CALL PAR   ; S2=SR
       D=X2-XD(2) ;  IF(D.LT.1.0) D=1.0
       X1=X2-D    ;  E0=X1     ; CALL PAR   ; S1=SR

       IF(S1.LT.S2)GO TO 8

       X3=X2+D    ;  E0=X3     ; CALL PAR   ; S3=SR

       IF(S3.LT.S2)GO TO 20

       IF(S1.LT.S3)GO TO 4

       T=X2      ;   X2=X3   ; X3=T
       T=S2      ;   S2=S3   ; S3=T
       GO TO 20

4      T=X1      ;   X1=X3   ; X3=X2     ; X2=T
       T=S1      ;   S1=S3   ; S3=S2     ; S2=T
       GO TO 20

8      X3=X1-D   ;   E0=X3   ; CALL PAR  ; S3=SR

       IF(S3.LT.S1)GO TO 16

       IF(S2.LT.S3)GO TO 12

       T=X1      ;   X1=X2   ; X2=X3     ; X3=T
       T=S1      ;   S1=S2   ; S2=S3     ; S3=T
       GO TO 20

12     T=X1      ;   X1=X3   ; X3=T
       T=S1      ;   S1=S3   ; S3=T
       GO TO 20

16     T=X1      ;   X1=X2   ; X2=T
       T=S1      ;   S1=S2   ; S2=T

20     DO 24  K=1,30

       Z1=X1-X3   ; Z2=X2-X3 ; Q1=(S1-S3)/Z1 ; Q2=(S2-S3)/Z2
```

```
      D=(Z2*Q1-Z1*Q2)/(Q2-Q1)*.5
      E0=X3-D     ;  CALL PAR

      IF(ABS(D).LT..001)RETURN

      X1=X2       ;  X2=X3      ;  X3=E0
      S1=S2       ;  S2=S3      ;  S3=SR

   24 CONTINUE

      RETURN
      END
```

C4. Subroutine PAR

Using a least-squares method, this subroutine calculates the parameters for the mathematical model.

We know the admittance relations

$$\sigma = g_0 + j\omega C_\infty + \frac{j\omega C_1}{1+j\omega C_1/g_1} + \frac{j\omega C_2}{1+j\omega C_2/g_2} \tag{5.1}$$

$$\hat{\sigma} = \frac{j\omega C_0 \sigma}{\sigma + j\omega C_0}\ ; \tag{5.2}$$

$\tau_1 = C_1/g_1$; let $T_1 = 2\pi\tau_1$, then $\omega\tau_1 = 2\pi f\tau_1 = fT_1$.

Let $f_0 = \frac{g_0}{2\pi}$ then

$\frac{\sigma}{j\omega} = p - jq,\quad \frac{\hat{\sigma}}{j\omega} = X - jY$

where p and q are the normalized (A1) permittivity and conductivity of the ice and X, Y are those of the test cell.

$$p = C_\infty + \frac{C_1}{1+T_1^2f^2} + \frac{C_2}{1+T_2^2f^2} \tag{5.3a}$$

$$q = \frac{f_0}{f} + \frac{C_1T_1f}{1+T_1^2f^2} + \frac{C_2T_2f}{1+T_2^2f^2}\ . \tag{5.3b}$$

Expressing p, q in terms of the blocking-capacitor response

$$p = \frac{E_0[(E_0-X)X-Y^2]}{(E_0-X)^2+Y^2}$$

$$q = \frac{E_0^2Y}{(E_0-X)^2+Y^2}\ ,$$

and, conversely

$$X = \frac{E_0[(E_0+p)p+q^2]}{(E_0+p)^2+q^2}$$

$$Y = \frac{E_0^2q}{(E_0+p)^2+q^2}$$

We apply a p-fit method; the p relation involves four Debye parameters, if we chose two Debye elements for the mathematical model.

$$p = \frac{C_1}{1+T_1^2f^2} + \frac{C_2}{1+T_2^2f^2} + C_\infty \tag{5.3a}$$

where C_∞ is assumed known

let $\alpha_1 = T_1^2$, $\alpha_2 = T_2^2$, $r = p - C_\infty$

$$r = p - C_\infty = \frac{C_1}{1+T_1^2f^2} + \frac{C_2}{1+T_2^2f^2}$$

$$r = \frac{C_1}{1+\alpha_1 f^2} + \frac{C_2}{1+\alpha_2 f^2}$$

$$r = \frac{C_1(1+\alpha_2 f^2)+C_2(1+\alpha_1 f^2)}{(1+\alpha_1 f^2)(1+\alpha_2 f^2)}$$

$$r(1+\alpha_1 f^2)(1+\alpha_2 f^2) = C_1+\alpha_2 C_1 f^2+C_2+\alpha_1 C_2 f^2$$

$$r(1+\alpha_1 f^2+\alpha_2 f^2+\alpha_2\alpha_1 f^4) = C_1+C_2+(\alpha_1 C_2+\alpha_2 C_1)f^2$$

$$r = C_1+C_2+(\alpha_1 C_2+\alpha_2 C_1)f^2-(\alpha_1+\alpha_2)rf^2-\alpha_1\alpha_2 rf^4$$

Let $C_1+C_2 = \beta_1$, $\alpha_1 C_2+C_1\alpha_2 = \beta_2$, $\alpha_1+\alpha_2 = \beta_3$, $\alpha_1\alpha_2 = \beta_4$

$$\beta_1+\beta_2 f^2-\beta_3 rf^2-\beta_4 rf^4 = r \tag{6.3}$$

Given a data set $\{ (f_i, p_i), i = 1. n \}$

$$r_i = p_i - C_\infty .$$

Using a least squares method involving more than 4 data points

Let $e_i = \beta_1+\beta_2-\beta_3 r_i f_i^2-\beta_4 r_i f_i^4-r_i$

The least-squares criterion requires that

$$S = e_1^2+e_2^2+ \ldots + e_N^2 = \sum_{i=1}^{N} e_i^2$$

$$= \sum_{i=1}^{N}(\beta_1+\beta_2 f_i^2-\beta_3 r_i f_i^2-\beta_4 r_i f_i^4-r_i)^2$$

be a minimum. N is the number of data. We reach the minimum by proper choice of the parameters β_1, β_2, β_3, andβ_4, so they are the variables of the problem. At a minimum for S, the four partial derivatives $\frac{\partial S}{\partial \beta_1}$, $\frac{\partial S}{\partial \beta_2}$, $\frac{\partial S}{\partial \beta_3}$ and $\frac{\partial S}{\partial \beta_4}$ will be zero. Hence, remembering that the r_i and f_i are data points unaffected by our choice of the values for β_1, β_2, β_3, andβ_4 we have

$$\frac{\partial S}{\partial \beta_1} = \sum_{i=1}^{N} 2\times(\beta_1+\beta_2 f_i^2-\beta_3 r_i f_i^2-\beta_4 r_i f_i^4-r_i) = 0$$

$$\frac{\partial S}{\partial \beta_2} = \sum_{i=1}^{N} 2\times f_i^2(\beta_1+\beta_2 f_i^2-\beta_3 r_i f_i^2-\beta_4 r_i f_i^4-r_i) = 0$$

$$\frac{\partial S}{\partial \beta_3} = -\sum_{i=1}^{N} 2\times r_i f_i^2(\beta_1+\beta_2 f_i^2-\beta_3 r_i f_i^2-\beta_4 r_i f_i^4-r_i) = 0$$

$$\frac{\partial S}{\partial \beta_4} = -\sum_{i=1}^{N} 2\times r_i f_i^4(\beta_1+\beta_2 f_i^2-\beta_3 r_i f_i^2-\beta_4 r_i f_i^4-r_i) = 0$$

Dividing each of these equations by 2 or -2 and expanding the summation, we get the so-called normal equations. The normal equations then become

$$\begin{bmatrix} N & \sum f_i^2 & -\sum r_i f_i^2 & -\sum r_i f_i^4 \\ \sum f_i^2 & \sum f_i^4 & -\sum r_i f_i^4 & -\sum r_i f_i^6 \\ \sum r_i f_i^2 & \sum r_i f_i^4 & -\sum r_i^2 f_i^4 & -\sum r_i^2 f_i^6 \\ \sum r_i f_i^4 & \sum r_i f_i^6 & -\sum r_i^2 f_i^6 & -\sum r_i^2 f_i^8 \end{bmatrix} \begin{bmatrix} \beta_1 \\ \beta_2 \\ \beta_3 \\ \beta_4 \end{bmatrix} = \begin{bmatrix} \sum r_i \\ \sum f_i^2 \times r_i \\ \sum r_i f_i^2 \times r_i \\ \sum r_i f_i^4 \times r_i \end{bmatrix}$$

where all summations are over i from 1 to N.

If the matrix of coefficients, the matrix of unknowns, and the matrix on the right are denoted by A, B, and G, respectively, then the normal equations can be written symbolically as the matrix equation

$$A\,B = G$$

Computational Summary for Curve-smoothing by Least Squares Polynomial

Step 1. Input, Read

N = Number of data pairs

(f_i, r_i) = data pairs (i =1, N)

Step 2. Generate terms for constructing normal equations, calculate the coefficients of A and G.

Step 3. Form normal matrix A and column matrix. calculate the coefficients of A and G.

Step 4. Solve normal equations AB = G

Step 5. Output coefficients B_k (k=1,N) of least-squares polynomial.

Using a point fit method

From

$$\beta_1 + \beta_2 f_i^2 - \beta_3 r_i f_i^2 - \beta_4 r_i f_i^4 = r_i, \tag{6.3}$$

we have 4 unknowns so that we need to have four data points to solve this equation. Substituting $\{(f_i, r_i),\ i = 1, 4\}$ into the equation we can get a 4 × 4 matrix equation

$$\begin{bmatrix} 1 & f_1^2 & -r_1 f_1^2 & -r_1 f_1^4 \\ 1 & f_2^2 & -r_2 f_2^2 & -r_2 f_2^4 \\ 1 & f_3^2 & -r_3 f_3^2 & -r_3 f_3^4 \\ 1 & f_4^2 & -r_4 f_4^2 & -r_4 f_4^4 \end{bmatrix} \begin{bmatrix} \beta_1 \\ \beta_2 \\ \beta_3 \\ \beta_4 \end{bmatrix} = \begin{bmatrix} r_1 \\ r_2 \\ r_3 \\ r_4 \end{bmatrix}$$

From the preceding it is seen that the matrix equation AB = G may be solved either by computing the least-squares polynomial for a set of data pairs (f_i, r_i) (i=1, N) using subroutine PAR, or by point fit to the selected set of data pairs (f_i, r_i) (i=1, 4).

The solutions β_1 , β_2 , β_3 , β_4 are obtained from the relations (Eqs. 6.3a to

6.3d) : $C_1+C_2 = \beta_1$, $\alpha_1 C_2+\alpha_2 C_1 = \beta_2$, $\alpha_1+\alpha_2 = \beta_3$, $\alpha_1\alpha_2 = \beta_4$; since we know $\alpha_2 = \beta_3-\alpha_1$, substitute into $\alpha_1\alpha_2 = \beta_4$; then

$$\alpha_1(\beta_3-\alpha_1) = \beta_4$$

$$-\alpha_1^2+\beta_3\alpha_1 = \beta_4$$

$$\alpha_1^2-\beta_3\alpha_1+\beta_4 = 0 \text{ , and}$$

$$\alpha_1 = \frac{\beta_3}{2}+\sqrt{(\frac{\beta_3}{2})^2-\beta_4}\,, \quad \alpha_2 = \beta_3-\alpha_1.$$

The parameters of the mathematical model are:

$$T_1 = \sqrt{\alpha_1}$$

$$T_2 = \sqrt{\alpha_2}$$

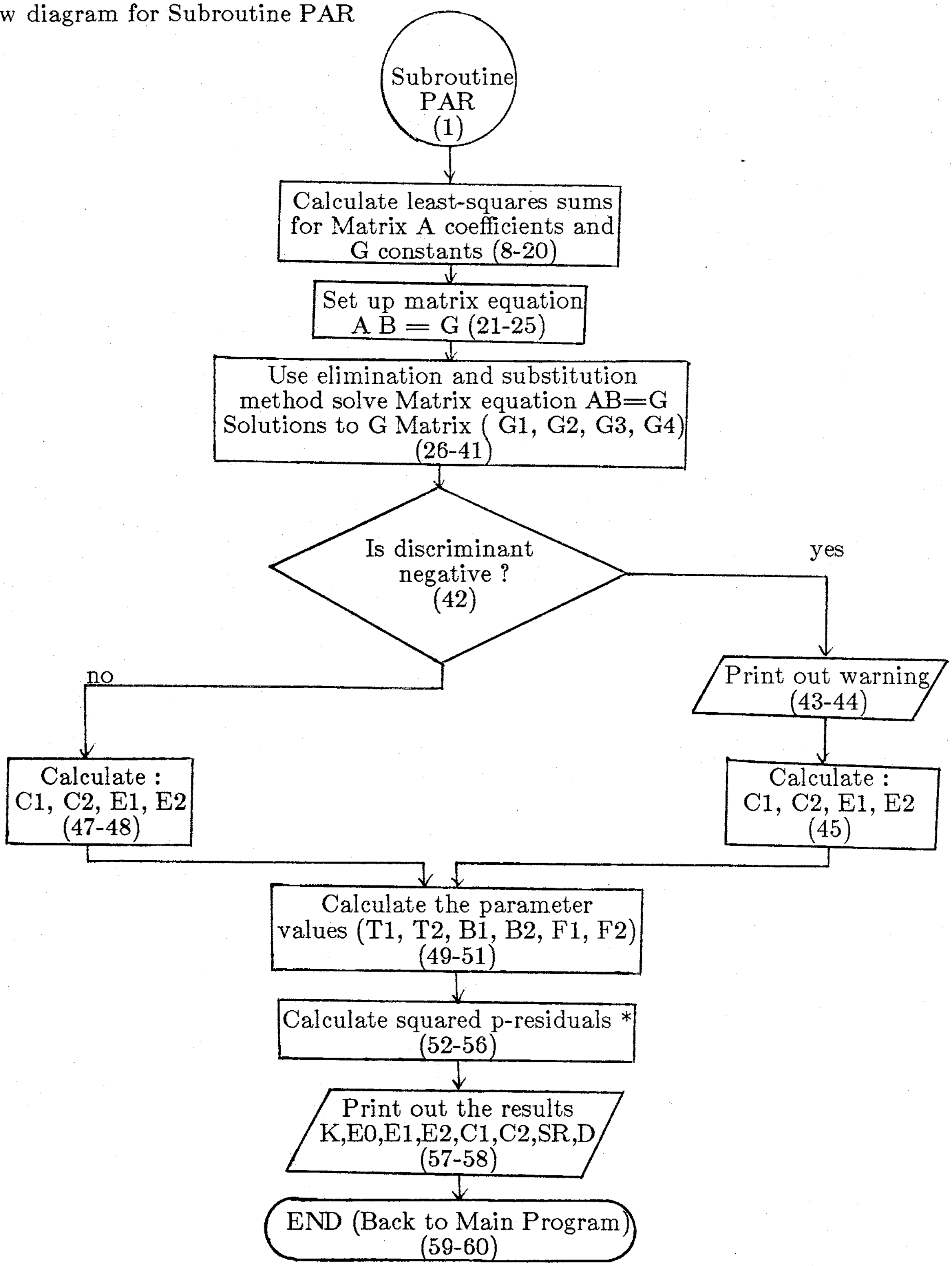
$$C_1 = \frac{(\beta_2-\alpha_2\beta_1)}{(\alpha_1-\alpha_2)}$$

$$C_2 = \beta_1-\epsilon_1 \text{ .}$$

T_1 , T_2 , C_1 , C_2 are model parameters. Substituting these model parameters into the q function we can calculate f_0 (see subroutine FOF).

The following pages show the flow diagram and list the subroutine.

Flow diagram for Subroutine PAR



* Only in LS2M

PAR subroutine listing

```
C     PAR subroutine
C     Computesdispersion parameters E1, E2, T1, T2
C     By least-squares fit between measured and computed
C     X, Y values at a number of measurement frequencies.

      SUBROUTINE PAR
      COMMON /A/NDAT,II,FD(30),XD(30),YD(30),SND,SF2,SF4,MM
      COMMON /C/E0,E02,EI,E1,T1,B1,C1,E2,T2,B2,C2,F0,SR,F1,F2

C     LEAST SQUARES SUMS

      SR = 0.;      SF2R = 0.;     SF4R = 0.;     SF6R = 0.
      SF2R2 = 0.;   SF4R2 = 0.;    SF6R2 = 0.;    SF8R2 = 0.

      DO 200 I = II,NDAT,MM
      F2 = FD(I)**2;              R = PF(E0,XD(I),YD(I)) - EI
      F2R = F2*R;                 F4R = F2*F2R
      F2R2 = F2R*R;               F4R2 = F4R*R
      F6R2 = F2*F4R2
      SR = SR + R;                SF2R = SF2R + F2R
      SF4R = SF4R + F4R;          SF6R = SF6R + F2*F4R
      SF2R2 = SF2R2 + F2R2;       SF4R2 = SF4R2 + F4R2
      SF6R2 = SF6R2 + F6R2
  200 SF8R2 = SF8R2 + F2*F6R2

C     MATRIX COEFFICIENTS AND CONSTANTS

      A11 = SND; A12 = SF2; A13 = - SF2R; A14 = - SF4R; G1 = SR
      A21 = SF2; A22 = SF4; A23 = - SF4R; A24 = - SF6R; G2 = SF2R
      A31 = SF2R; A32 = SF4R; A33 = - SF4R2; A34 = - SF6R2; G3 = SF2R2
      A41 = SF4R; A42 = SF6R; A43 = - SF6R2; A44 = - SF8R2; G4 = SF4R2

C     SOLUTION FOR PARAMETERS

      A41 = A41/A44;  A42 = A42/A44;  A43 = A43/A44;   G4 = G4/A44
      A11 = A11 - A14*A41;        A12 = A12 - A14*A42
      A13 = A13 - A14*A43;        G1 = G1 - A14*G4
      A21 = A21 - A24*A41;        A22 = A22 - A24*A42
      A23 = A23 - A24*A43;        G2 = G2 - A24*G4
      A31 = A31 - A34*A41;        A32 = A32 - A34*A42
      A33 = A33 - A34*A43;        G3 = G3 - A34*G4

      A31 = A31/A33;      A32 = A32/A33;      G3 = G3/A33
      A11 = A11 - A13*A31;  A12 = A12 - A13*A32;  G1 = G1 - A13*G3
      A21 = A21 - A23*A31;  A22 = A22 - A23*A32;  G2 = G2 - A23*G3

      A21 = A21/A22;              G2 = G2/A22
      A11 = A11 - A12*A21;        G1 = (G1 - A12*G2)/A11

      G2 = G2 - A21*G1;    G3 = G3 - A31*G1;    G4 = G4 - A41*G1
      G3 = G3 - A32*G2;    G4 = G4 - A42*G2;    G4 = G4 - A43*G3
```

```
      G3H = G3*.5;              D = G3H**2 - G4
      IF(D.GT.0.) GO TO 220

      WRITE(3,210)
  210 FORMAT('0NEGATIVE DISCRIMINANT')
      E1 = G1;    C1 = G3H;    E2 = 0.;    C2 = 0.
      GO TO 230

  220 C1 = G3H + SQRT(D);        C2 = G3 - C1
      E2 = (G2 - C2*G1)/(C1 - C2);        E1 = G1 - E2

  230 T1 = SQRT(ABS(C1));        T2 = SQRT(ABS(C2))
      B1 = E1*T1;                B2 = E2*T2
      F1=1./T1  ;                F2 = 1./T2

C     SUM OF SQUARED RESIDUALS

      SR = 0.
      DO 240 I = II,NDAT,MM
      FF = FD(I)**2
  240 SR = SR + (E1 / (1. + C1*FF) + E2 / (1. + C2*FF) + EI
      &      - PF(E0,XD(I),YD(I)))**2

      WRITE(3,250)K,E0,E1,E2,C1,C2,SR,D
  250 FORMAT(1x,I2,f12.6,6(F12.4))
      RETURN
      END
```

C5. Subroutine SEC

This subroutine uses a secant method to extrapolate E0 from low-frequency measurements. SEC interacts with subroutine PAR (App. C4) to minimize the sum of p-residuals derived from a small number of pre-selected measuring points.

First initiation step

Compute an initial value, ET, of E0 by two-point extrapolation (App. D2).

Next, this value ET is used to compute parameters and the sum of p-residuals, RR, from a few selected measuring points (IS, IE). Note that, to accomplish this, PAR is slightly different from the version used elsewhere (App. C4). The listing of this PAR version is therefore given with program LS2P (App. D8).

Second initiation step

This second initiation step consists of a three-point extrapolation of E0 (See App. D2). The difference D = ET-E0 is then computed and printed, along with an index, K = 0 and with the parameter values computed previously.

Third step : iteration

A Do-Loop with a maximum of 8 iterations (Statement 19) is used next to refine E0 and to minimize the sum of p-residuals (henceforth called SR) of the points (IS, IE) initially chosen.

First, PAR is called to compute parameters and SR, using the E0 derived from three-point extrapolation.

Next, a new D is computed from the previous D, RR, and SR:

$$D = D*SR/(RR-SR),$$

(Statement 21).

Thirdly, a new E0 is obtained

$$E0 = E0 - D,$$

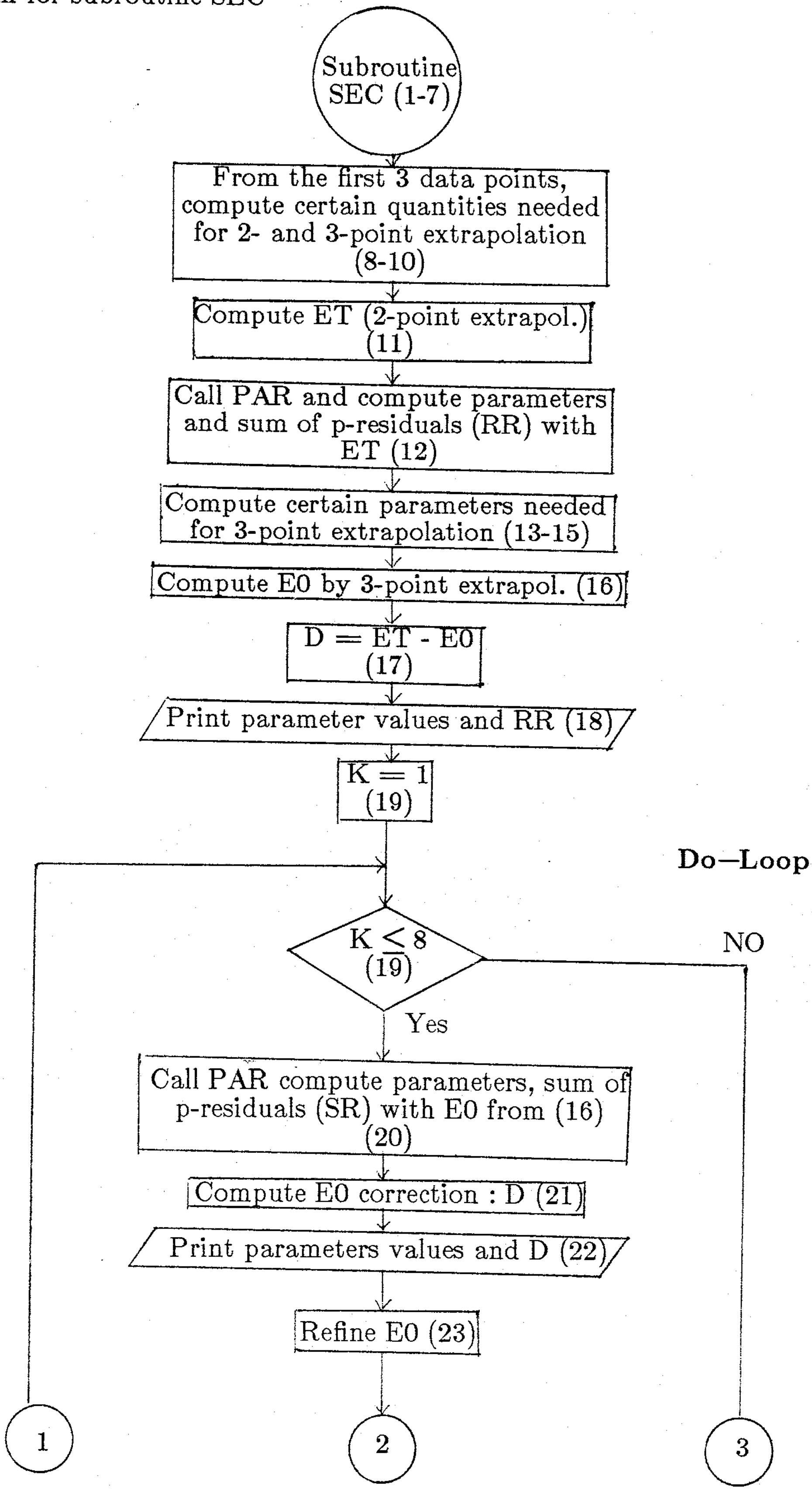
(Statement 23). If the absolute value of D was smaller than a selected tolerance (0.0005) the Do-Loop is terminated.

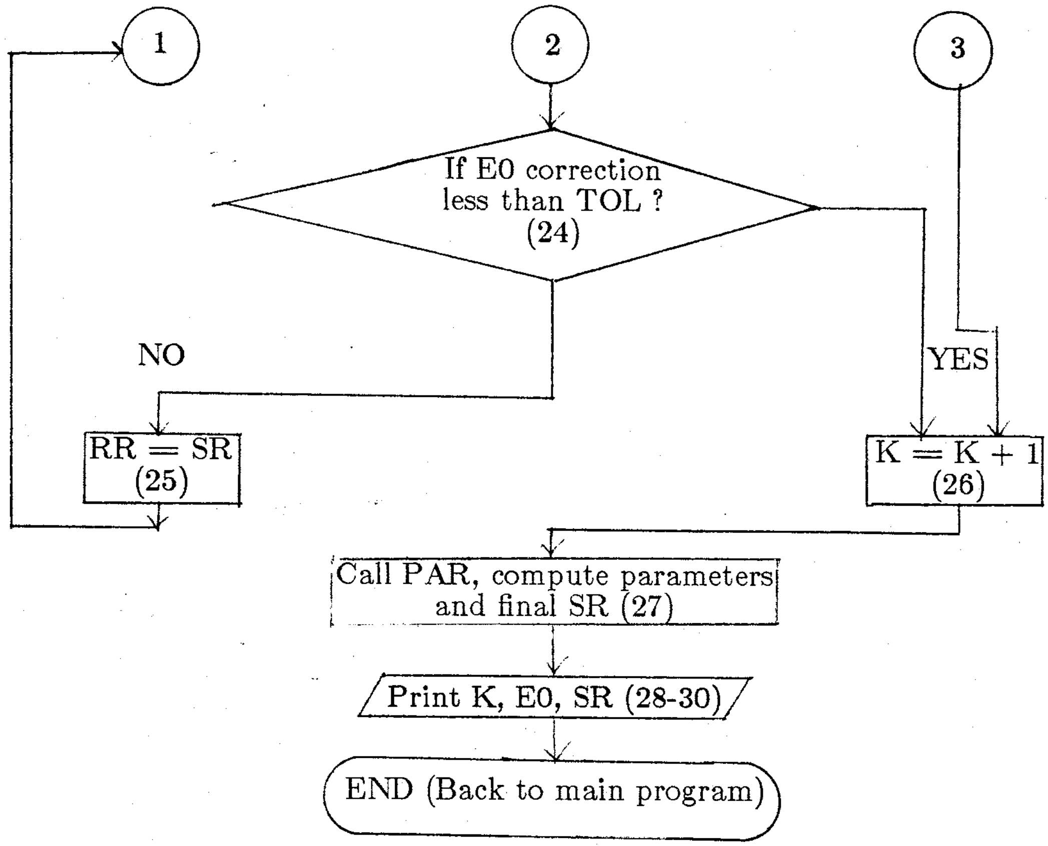
Fourth step : final parameters

PAR is called for one last time (Statement 27) to compute final parameters and SR. The final values of K, E0, SR are printed out before control returns to the main program.

The following pages show the flow diagram and list the subroutine.

Flow diagram for subroutine SEC




1
2
3
If E0 correction less than TOL ? (24)
NO
YES
RR = SR (25)
K = K + 1 (26)
Call PAR, compute parameters and final SR (27)
Print K, E0, SR (28-30)
END (Back to main program)

SEC subroutine listing

```
C      SEC subroutine
C      Uses a secant method to extrapolate E0

       SUBROUTINE SEC
       COMMON /A/NDAT,II,FD(30),XD(30),YD(30),SND,SF2,SF4,MM
       COMMON /C/E0,E02,EI,E1,T1,B1,C1,E2,T2,B2,C2,F0,SR,F1,F2
       WRITE(3,200)
       k = 0
       A12 = FD(1)**2  ; X1 = XD(1)    ; A13 = X1*A12
       A22 = FD(2)**2  ; X2 = XD(2)    ; A23 = X2*A22
       A32 = FD(3)**2  ; X3 = XD(3)    ; A33 = X3*A32

       ET = (A23*X1 - A13*X2) / (A23 - A13)
       E0 = ET  ;  CALL PAR   ;  RR = SR

       A31 = 1. / A33    ; A32 = A32 / A33  ; X3 = X3 / A33
       A11 = 1. - A13*A31; A12 = A12 - A13*A32  ;  X1 = X1 - A13*X3
       A21 = 1. - A23*A31  ; A22 = A22 - A23*A32  ; X2 = X2 - A23*X3
       E0 = (A22*X1 - A12*X2) / (A11*A22 - A12*A21)
       D = ET - E0
       WRITE(3,210)K,ET,E1,E2,C1,C2,SR,D

       DO 220 K = 1,8

       CALL PAR

       D = D*SR / (RR - SR)
       WRITE(3,210)K,E0,E1,E2,C1,C2,SR,D

       E0 = E0 - D
       IF(ABS(D).LT.(.0005))GO TO 230

  220  RR = SR
  230  K = K + 1

       CALL PAR
       WRITE(3,210)K,E0,SR
  200  FORMAT(/2X,'K',6X,'E0',10X,'E1',10X,'E2',11X,'C1',10X,'C2',
       1 10X,'SR',10X,'D'/)
  210  FORMAT(1X,I2,f12.6,6(F12.4))
       RETURN
       END
```

Table V List of Subroutines

CALRSD	Computes residuals between "Calculated" and "Measured" values, respectively, of x, y, p, q, and fq, RMS deviations of xy and fq.
F0F	Computes the dc conductance parameter from measurement-derived q-values (Eq. 5.4b) and computed values E, T (Eq. 6.8) at each frequency, then averages them for display as one value.
MIN	Computes an E0 value by minimizing the sums of deviations between measured x, y values and those derived with E0 values deviating systematically from an initially assumed value.
PAR	Computes dispersion parameters E1, E2, T1, T2 by least-squares fit between measured and computed x, y values at a number of measurement frequencies.
SEC	Uses a secant method to extrapolate E0

Appendix D : Least-Squares Fitting Programs

D1. Introduction

All programs whose designation begins with letters LS (Table VI) compute dispersion parameters with a least-squares fit of a set of data points (subject to restrictions discussed in section 6.7). This is done in subroutine PAR.

DC conductance is computed in subroutine F0F.

Data to evaluate goodness of fit are computed in subroutine CALRSD.

The numeral "2" following the letters LS indicates the number of Debye elements of the equivalent circuit (Section 5).

The differences between these LS programs are in the method of E0 evaluation discussed in Section 6 (see Table V for an overview), and as shown in the following list.

1. LS2X2 : Fitting program for data with two Debye elements (where E0 is extrapolated from the first two data points).
2. LS2X3 : Fitting program for data with two Debye elements (where E0 is extrapolated from the first three data points).
3. LS2X4 : Fitting program for data with two Debye elements (where E0 is extrapolated from the first four data points).
4. LS2F : Fitting program for data with two Debye elements (where E0 is fixed).
5. LS2M : Fitting program for data with two Debye elements (where E0 is found by minimizing sum of residuals).
6. LS2P : Fitting program for data with two Debye elements. E0 is found with a secant method which minimizes the sum of residuals calculated from some chosen points.

7. LS2PQ : Fitting program for data with two Debye elements (where E0 is zero; i.e. no blocking layers used).

These programs are easily adapted for use with a single Debye element.

Table VI. List of Inversion Programs

Designation	Method to find: Dispersion parameters	Method to find: E0	Debye elements	Remarks
LS1M LS2M	Minimize deviations by least-squares (Subroutine PAR)	Minimize deviations of a sum of squared p-residuals. (Subroutine MIN)	1 2	
LS2F	Least-squares fit	Fixed and predetermined	2	
LS2PQ	Least-squares fit	No blocking layers (No E0)	2	X=P, Y=Q
LS1P LS2P	Least-squares fit Least-squares fit	Secant extrapolation Secant extrapolation	1 2	
LS1X(2) LS2X(2)	Least-squares fit Least-squares fit	Two-point extrapolation Two-point extrapolation	1 2	
LS1X(3) LS2X(3)	Least-squares fit Least-squares fit	Three-point extrapolation Three-point extrapolation	1 2	
LS1X(4) LS2X(4)	Least-squares fit Least-squares fit	Four-point extrapolation Four-point extrapolation	1 2	
PF2M	Point fit on P-values	Least-squares minimiz.	2	
PF2P	Point fit on P-values	Secant extrapolation	2	
PF2X(2)	Point fit on P-values	2-point extrapolation	2	
PF2X(3)	Point fit on P-values	3-point extrapolation	2	
PF2X(4)	Point fit on P-values	4-point extrapolation	2	
PF2F	Point fit on P-values	Fixed and predetermined	2	

D2. E_0 evaluation - point fit (Low-frequency approximation)

Start with

$$p = \frac{C_1}{1+T_1^2f^2}+\frac{C_2}{1+T_2^2f^2}+C_\infty \qquad (5.3a)$$

$$p = \frac{E_0[E_0-X)X-Y^2]}{(E_0-X)^2+Y^2}. \qquad (5.4a)$$

From the above equations, let $p = a+\frac{b}{1+cf^2}$, then :

$$p = a+\frac{b}{1+cf^2} = \frac{E_0[(E_0-X)X-Y^2]}{(E_0-X)^2+X^2}.$$

Multiply both sides with $1+cf^2$;

$$p(1+cf^2) = a(1+cf^2)+b$$

$$p+pcf^2 = a+acf^2+b$$

$$(a+b)+acf^2-cpf^2-p = 0 .$$

Let $a+b = \alpha$, $ac = \beta$,

redefine $f_i = f_i^2$, then

$$\alpha+\beta f_i-cpf_i = p_i .$$

Solve this augmented matrix of equations, eliminate α , β and c to obtain an equation involving the data and E_0. To evaluate the E_0 values use extrapolation by 2-, 3-, or 4 points.

This method extrapolates low-frequency x-values to obtain an estimate of E_0, ($x \rightarrow E_0$ as $f \rightarrow 0$), values of y are not involved. From circuit theory, x is an even function of f. In this application, rational approximation of x(f) at small f is more accurate for extrapolation than polynomials.

Using the 2, 3, or 4 data points at the lowest frequencies, the following extrapolation formulas are obtained :

(1) Two points : $X_2(f) = \frac{E_0}{1+\alpha_2 f}$. LS2X2 is a program based on 2-point extrapolation of E_0.

(2) Three points : $X_3(f) = \frac{E_0(1+\beta_3 f^2)}{1+\alpha_3 f^2}$. LS2X3 is a program based on 3-point extrapolation of E_0.

(3) Four points : $x_4(f) = \frac{E_0(1+\beta_4 f^2)}{1+\alpha_4 f^2+\gamma_4 f^2}$. LS2X4 is a program based on 4-point extrapolation of E_0.

From the above three conditions, the set of linear equations obtained by substituting the appropriate number of data points in the relations is solved for E_0.

D3. LS2X2, LS2X3, LS2X4

These programs include a main program, three subroutines : PAR, CALRSD, FOF, and one function, PF. The equivalent circuit and mathematical model have been discussed in section 5. Our fitting parameters are EI, E0, E1, E2, T1, T2, and F0. In the main program we need to calculate the effective scaled dielectric constant of the driving capacitor (E0).

LS2X2 :

From the E_0 evaluation (Section D2) :

$$X_2(f) = \frac{E_0}{1+\alpha_2 f^2}. \tag{D.1}$$

We have 2 unknowns, which are E_0 and α_2, so that we need to have 2 points to fit. Substitute (X_1,f_1), (X_2,f_2) into Eq. (D.1), and evaluate E_0 by

$$E_0 = X_1 + \frac{(X_1-X_2)}{[\frac{X_2}{X_1}(\frac{f_2}{f_1})^2-1]}. \tag{D.2}$$

LS2X3 :

From the E_0 evaluation (Section D2) :

$$X_3(f) = \frac{E_0(1+\beta_3 f^2)}{1+\alpha_3 f^2}. \tag{D.3}$$

Multiply Eq. (D.3) by $1+\alpha_3 f^2$, get

$$X_3(f) = E_0\beta_3 f^2 - X_3(f)\alpha_3 f^2 - E_0. \tag{D.4}$$

We have 3 unknowns, which are E_0, β_3, α_3, so we need to have 3 data points to fit. Let $E_0\beta_3 = H$, substitute (X_1,f_1), (X_2,f_2), (X_3,f_3) into Eq. (D.4), and compute E_0 by solving the matrix equation

$$\begin{bmatrix} f_1^2 & -X_1 f_1^2 & 1 \\ f_2^2 & -X_2 f_2^2 & 1 \\ f_3^2 & -X_3 f_3^2 & 1 \end{bmatrix} \begin{bmatrix} H \\ \alpha_3 \\ E_0 \end{bmatrix} = \begin{bmatrix} X_1 \\ X_2 \\ X_3 \end{bmatrix} \tag{D.5}$$

LS2X4 :

From the E_0 evaluation (Section D2) :

$$X_4(f) = \frac{E_0(1+\beta_4 f^2)}{1+\alpha_4 f^2+\gamma_4 f^4}. \tag{D.6}$$

Multiply Eq. (D.6) by $1+\alpha_4 f^2+\gamma_4 f^4$, get

$$E_0+E_0\beta_4 f^2-X_4(f)\alpha_4 f^2-X_4(f)\gamma_4 f^4 = X_4(f). \tag{D.7}$$

We have 4 unknowns, which are E_0, β_4, α_4, γ_4, so we need to have 4 data points to fit. Let $E_0\beta_4 = a$, substitute (X_1,f_1), (X_2,f_2), (X_3, f_3), (X_4,f_4) into Eq. (D.7), and evaluate E_0 by solving the following matrix equation

$$\begin{bmatrix} 1 & f_1^2 & -X_1f_1^2 & -X_1f_1^4 \\ 1 & f_2^2 & -X_2f_2^2 & -X_2f_2^4 \\ 1 & f_3^2 & -X_3f_3^2 & -X_3f_3^4 \\ 1 & f_4^2 & -X_4f_4^2 & -X_4f_4^4 \end{bmatrix} \begin{bmatrix} E_0 \\ a \\ \alpha_4 \\ \gamma_4 \end{bmatrix} = \begin{bmatrix} X_1 \\ X_2 \\ X_3 \\ X_4 \end{bmatrix} \tag{D.8}$$

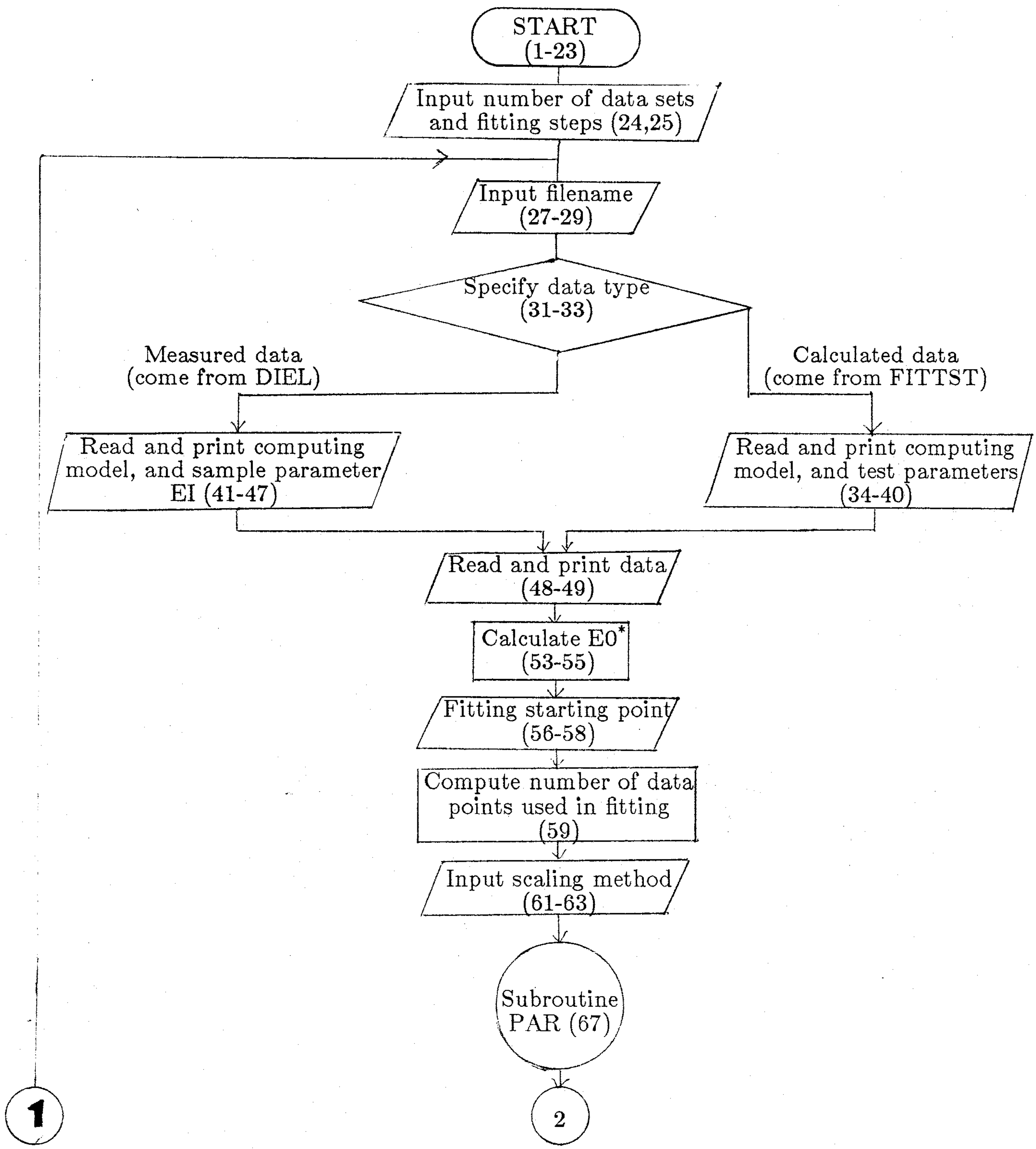
D4. PF FUNCTION

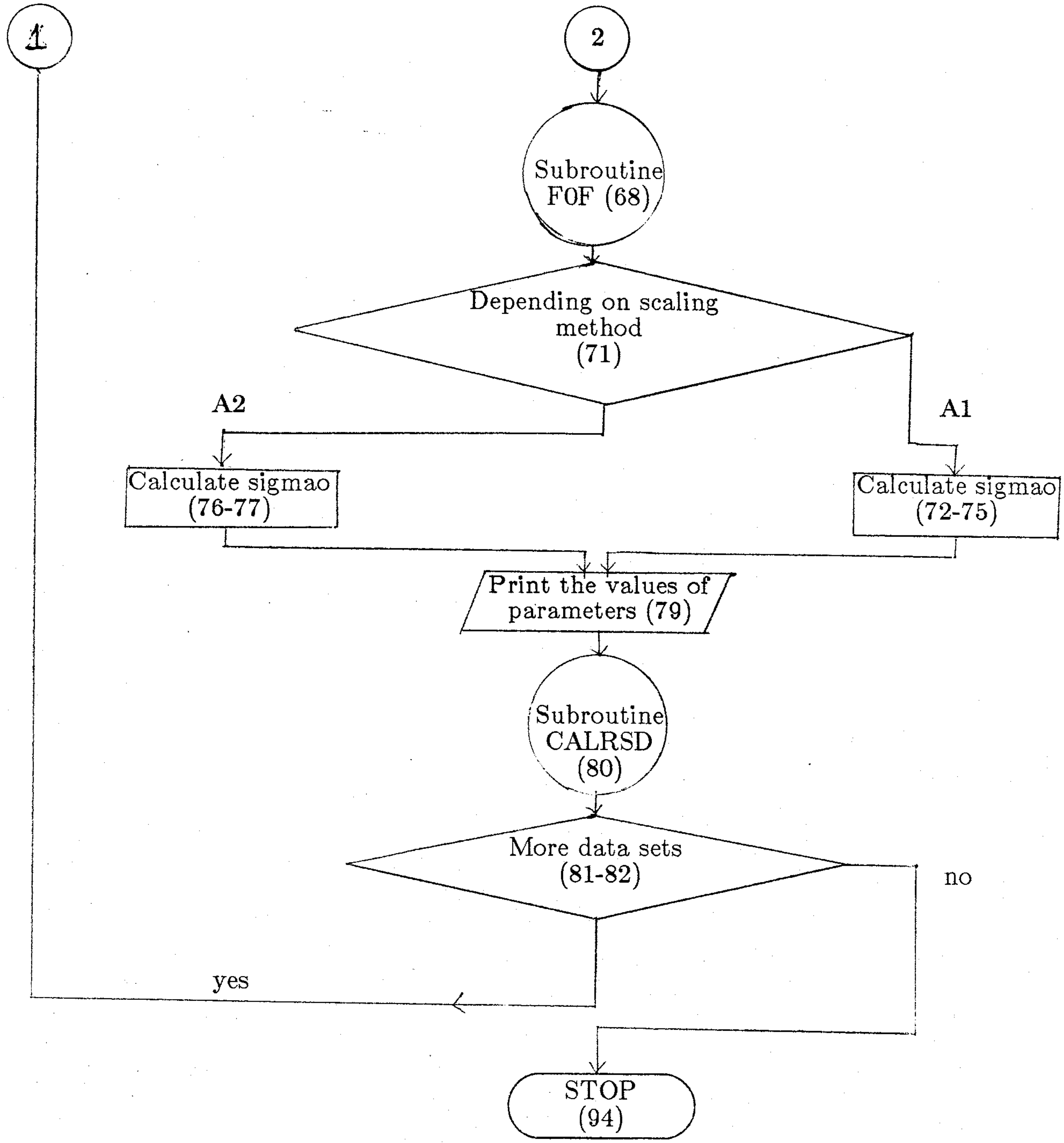
This subprogram calculates P. X, Y are measured data, from above we know E_0, so we can get P by

$$P = \frac{E_0[(E_0 - X)X - Y^2]}{[(E_0 - X)^2 + Y^2]} \tag{D.9}$$

D5. LS2X2 flow sheet and listing

The flow diagram for LS2X2





* E0 evaluation : LS2X3 uses a 3-point extrapolation. Substitute statements 53-55 by 353-360. LS2X4 uses a 4-point extrapolation. Substitute statements 53-55 by 453-472. LS2F uses a fixed and pre-determined value of E0. Substitute statements 53-55 by 553-555.

LS2X2 program listing

```
C     PROGRAM : LS2X2.FOR
C     Procedure to extract parameters F0, T, and Epsilon
C     E0, effective scaled value of driving capacitor.

C     Set of data containing frequencies [kHz],
C     real (XD), and imaginary (YD) components of the dielectric
C     spectrum.

C     Prior to inputting them into this program, XD and YD should be
C     scaled by one or other of two methods ;
C     Alternative 1 : Picofarads
C           X : Parallel capacitance
C           Y : Parallel conductance/omega

C     Alternative 2 : Nondimensional
C           X : Epsilon prime
C           Y : Epsilon double prime
C     Where :
C     OMEGA : 2*PI*FD(I),IN KILO RADIANS/SEC

C     Values for both scaling alternatives are directly taken
C     from output of DIEL.

      DOUBLE PRECISION DATIN,TEST
      CHARACTER*30 DESCR
      COMMON /A/NDAT,II,FD(30),XD(30),YD(30),SND,SF2,SF4,MM
      COMMON /C/E0,E02,EI,E1,T1,B1,C1,E2,T2,B2,C2,F0,SR,F1,F2

C     READ IN DATA INTO FD, XD, AND YD ARRAYS

      WRITE(5,*)' PLEASE INPUT NUMBER OF FILE SETS TO BE FITTED
     1 AND FITTING STEP '
      READ(5,*) NSET,MM
      K=0
   10 WRITE(5,*)' PLEASE INPUT FILE NAME '
      WRITE(3,20)
      READ(5,30)DATIN

      OPEN(UNIT=25,DEVICE='DSK',FILE=DATIN)
      WRITE(5,*)' Are these modelling data ? Type YES for " yes "
     1 & type NO for " no " '
      READ(5,30)TEST

      IF(TEST.EQ.'YES')THEN
            READ(25,30)DESCR
            READ(25,40)TE0,TE1,TE2,TT1,TT2,TF0,TEI
            WRITE(3,*)'    LS2X(2 POINT) Model '
            WRITE(3,50)DESCR
            WRITE(3,*)' THESE TEST DATA ARE GENERATED FROM FOLLOWING
     1        PARAMETERS : '
            WRITE(3,60)TE0,TF0,TEI,TE1,TE2,TT1,TT2
```

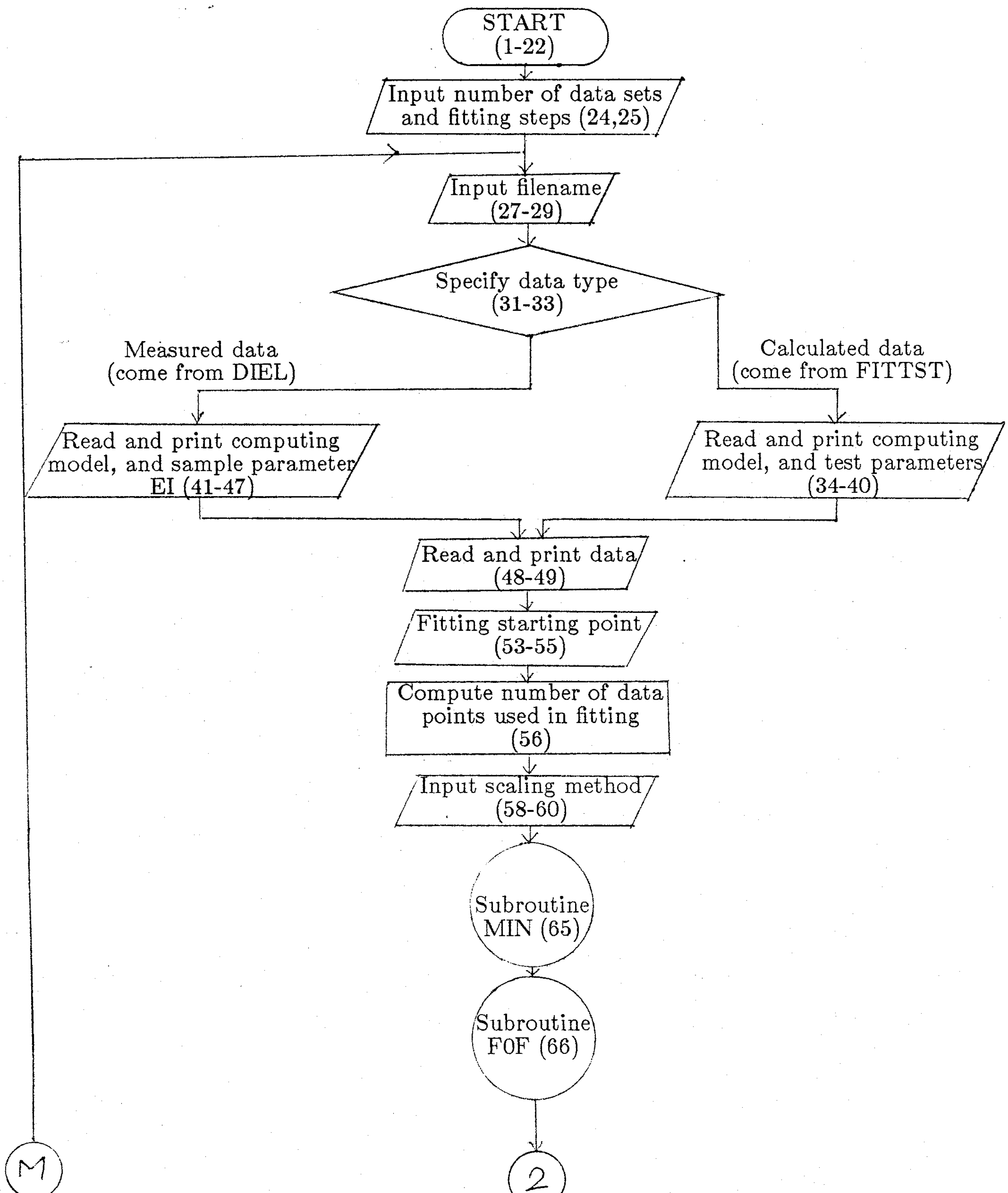
```
          EI = TEI
      ELSE
          READ(25,30)DESCR
          WRITE(3,*)'    LS2X(2 POINT) Model '
          WRITE(3,50)DESCR
          WRITE(5,*)' PLEASE INPUT " EI " '
          READ(5,*)EI
      ENDIF

      READ(25,70) NDAT
      READ(25,80) (FD(I), XD(I), YD(I), I=1,NDAT)
      CLOSE(UNIT=25)

      TPI = 6.2831853
      TPIK = TPI*1000

C     Using 2-point extrapolation evaluate E0

      X1 = XD(1)         ;    X2 = XD(2)
      E0=X1+(X1-X2)/(X2/X1*(FD(2)/FD(1))**2-1.0)

      WRITE(5,*)' PLEASE INPUT FITTING STARTING POINT '
      READ(5,*)II
      WRITE(3,90)II
      SND = (NDAT - II)/MM + 1
      SF2 = 0.      ;      SF4 = 0.

      WRITE(5,*)' Please input method for scaling the data, "A1" or "A2" '
      READ(5,30)SWITCH
      WRITE(3,95)SWITCH

      DO 100 I = II,NDAT,MM
      FF = FD(I)**2  ;      SF2 = SF2 + FF
  100 SF4 = SF4 + FF**2

      CALL PAR

      CALL F0F

      TAU1 = T1/TPIK
      TAU2 = T2/TPIK

      IF (SWITCH .EQ. 'A1' ) THEN
          WRITE(5,*) ' A1 method need input geometrical factor "A/L" '
          WRITE(5,*) ' for calculating Sigma0 '
          READ(5,*) AL
          SIGMA0=TPIK*1.0E-12*F0/AL
      ELSE
          SIGMA0=TPIK*F0*8.85E-14
      ENDIF
          WRITE(3,110) E0,F0,TAU1,E1,E2,TAU2,T1,T2,SIGMA0,B1,B2,EI,C1,C2,
     1 F1,F2
      CALL CALRSD
      K = K+1
```

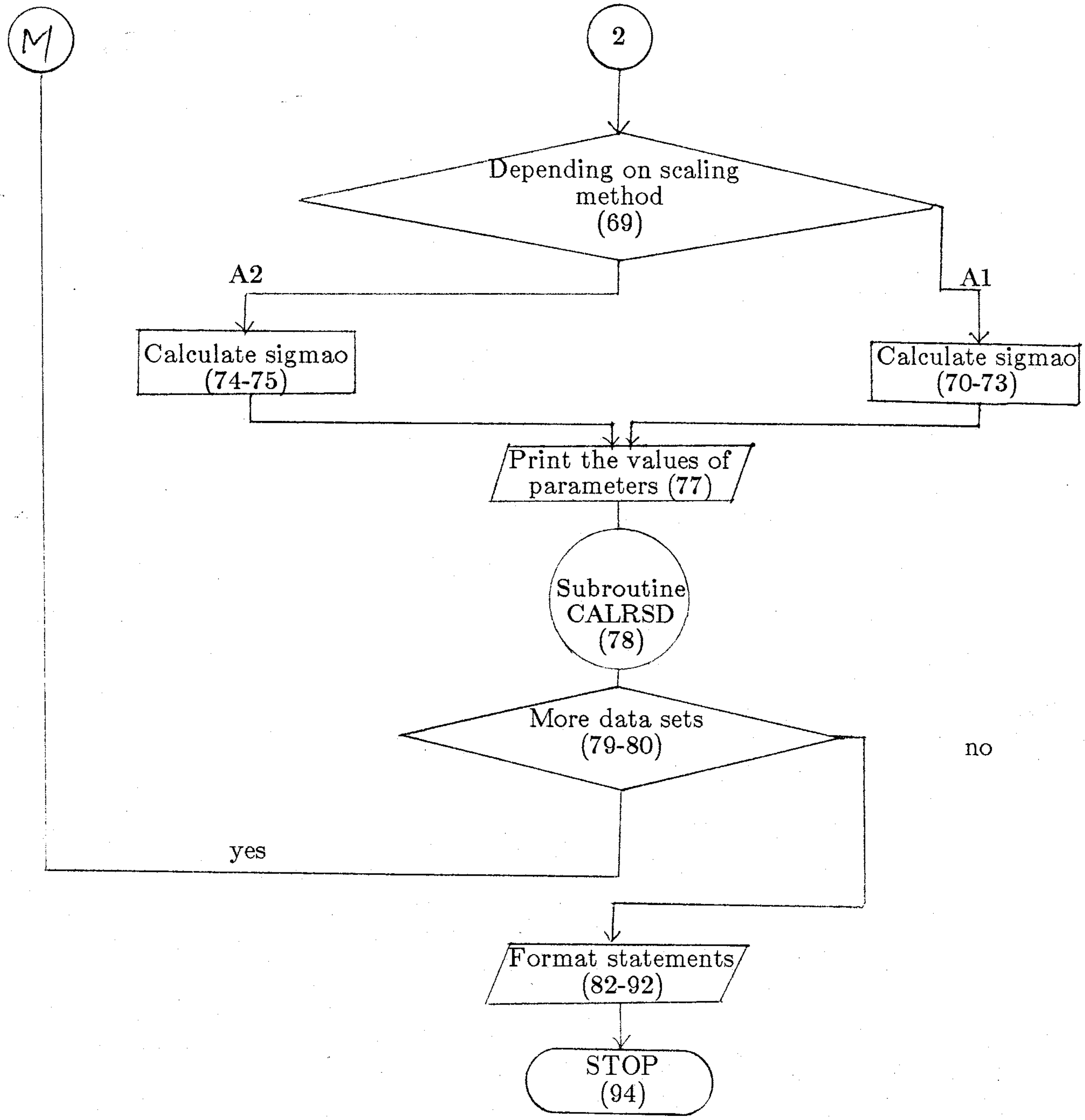
```
      IF(K.GE.NSET)STOP
      GO TO 10

20    FORMAT('1')
30    FORMAT(A)
40    FORMAT(7F)
50    FORMAT(A/)
60    FORMAT(/,7X,'E0 = ',F12.4,4X,'F0 = ',F12.4,4X,'EI = ',F12.4
     1,/7X,'E1 = ',F12.4,4X,'E2 = ',F12.4
     1,/7X,'T1 = ',F12.4,4X,'T2 = ',E12.4/)
70    FORMAT(I)
80    FORMAT(3F)
90    FORMAT(/2X,'FITTING STARTING POINT = ',I3/)
95    FORMAT(2X,'Scaling : Alternative ', 2A)
110   FORMAT(/,7X,'E0 = ',F12.4,4X,'F0 = ',F12.4
     1,4X,'TAU1=',E12.4/7X,'E1 = ',F12.4,4X,'E2 = ',F12.4
     1,4X,'TAU2=',E12.4/7X,'T1 = ',F12.4,4X,'T2 = ',F12.4
     1,4X,'SIGMA0=',E12.4/7X,'B1 = ',F12.4,4X,'B2 = ',F12.4,4X,
     1'EI= ',F12.4,/7X,'C1 = ',F12.4,4X,'C2 = ',F12.4/,7X,'F1 = '
     1,F12.4,4X,'F2 = ',F12.4)
      STOP
      END
```

```
C      Using 3-point extrapolation evaluate E0

       A12 = FD(1)**2   ;   X1 = XD(1)    ;  A13 = X1*A12
       A22 = FD(2)**2   ;   X2 = XD(2)    ;  A23 = X2*A22
       A32 = FD(3)**2   ;   X3 = XD(3)    ;  A33 = X3*A32

       A31 = 1. / A33    ; A32 = A32 / A33  ; X3 = X3 / A33
       A11 = 1. - A13*A31; A12 = A12 - A13*A32  ;  X1 = X1 - A13*X3
       A21 = 1. - A23*A31  ; A22 = A22 - A23*A32  ; X2 = X2 - A23*X3
       E0 = (A22*X1 - A12*X2) / (A11*A22 - A12*A21)


C      Using 4-point extrapolation evaluate E0

       I = 1       ; FF1 = FD(I)**2     ; X1 = XD(I)
       I = I + 1   ; FF2 = FD(I)**2     ; X2 = XD(I)
       I = I + 1   ; FF3 = FD(I)**2     ; X3 = XD(I)
       I = I + 1   ; FF4 = FD(I)**2     ; X4 = XD(I)

       A12 = FF1  ;  A13 = FF1*X1  ; A14 = FF1*A13  ; R1 = X1
       A22 = FF2  ;  A23 = FF2*X2  ; A24 = FF2*A23  ; R2 = X2
       A32 = FF3  ;  A33 = FF3*X3  ; A34 = FF3*A33  ; R3 = X3
       A42 = FF4  ;  A43 = FF4*X4  ; A44 = FF4*A43  ; R4 = X4

       A41 = 1.0/A44 ; A42 = A42/A44 ;  A43 = A43/A44  ; R4 = R4/A44
       A11 = 1.0 - A14*A41         ;  A12 = A12 - A14*A42
       A13 = A13 - A14*A43         ;  R1 = R1 - A14*R4

       A21 = 1.0 - A24*A41         ;  A22 = A22 - A24*A42
       A23 = A23 - A24*A43         ;  R2 = R2 - A24*R4

       A31 = 1.0 - A34*A41         ;  A32 = A32 - A34*A42
       A33 = A33 - A34*A43         ;  R3 = R3 - A34*R4

       A31 = A31/A33       ; A32 = A32/A33        ;  R3 = R3/A33
       A11 = A11 - A13*A31 ; A12 = A12 - A13*A32  ;  R1 = R1 - A13*R3
       A21 = A21 - A23*A31 ; A22 = A22 - A23*A32  ;  R2 = R2 - A23*R3

       E0 = (R1*A22 - R2*A12)/(A11*A22 - A12*A21)


C      Input a fixed and pre-determined value of E0

       WRITE(5,*)' PLEASE INPUT E0 '
       READ(5,*) E0
```

D6. LS2M flow sheet and listing

The flow diagram for LS2M




M
2
Depending on scaling method (69)
A2
A1
Calculate sigmao (74-75)
Calculate sigmao (70-73)
Print the values of parameters (77)
Subroutine CALRSD (78)
More data sets (79-80)
no
yes
Format statements (82-92)
STOP (94)

LS2M program listing

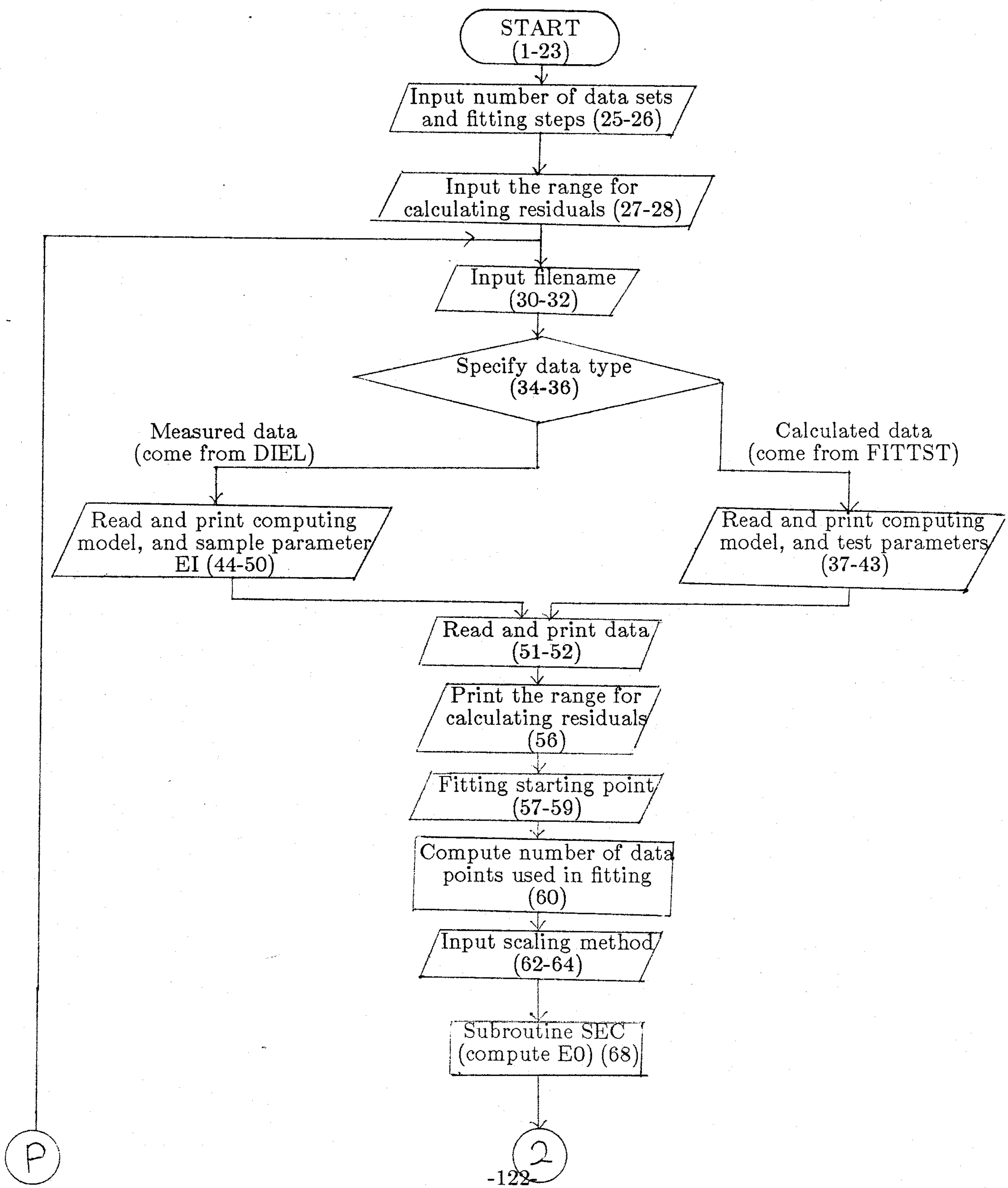
```
C     PROGRAM NAME : LS2M.FOR
C     Procedure to extract parameters F0, T, and Epsilon
C     E0, effective scaled value of driving capacitor.

C     Set of data containing frequencies [kHz],
C     real (XD), and imaginary (YD) components of the dielectric
C     spectrum.

C     Prior to inputting them into this program, XD and YD should be
C     scaled by one or other of two methods ;
C     Alternative 1 : Picofarads
C             X : Parallel capacitance
C             Y : Parallel conductance/omega

C     Alternative 2 : Nondimensional
C             X : Epsilon prime
C             Y : Epsilon double prime
C     Where :
C     OMEGA : 2*PI*FD(I),IN KILO RADIANS/SEC

C     Values for both scaling alternatives are directly taken
C     from output of DIEL.

      DOUBLE PRECISION DATIN,TEST
      CHARACTER*30 DESCR
      COMMON /A/NDAT,II,FD(30),XD(30),YD(30),SND,SF2,SF4,MM
      COMMON /C/E0,E02,EI,E1,T1,B1,C1,E2,T2,B2,C2,F0,SR,K,D,F1,F2

C     READ IN DATA INTO FD, XD, AND YD ARRAYS

      WRITE(5,*)' Please input number of file sets to be fitted
     1  and fitting step '
      READ(5,*) NSET,MM
      K=0
10    WRITE(5,*)' PLEASE INPUT FILE NAME '
      WRITE(3,20)
      READ(5,30)DATIN

      OPEN(UNIT=25,DEVICE='DSK',FILE=DATIN)

      WRITE(5,*)' Are these modelling data ? Type YES for " yes "
     & type NO for " no " '
      READ(5,30)TEST
      IF(TEST.EQ.'YES')THEN
      READ(25,30)DESCR
      READ(25,40)TE0,TE1,TE2,TT1,TT2,TF0,TEI
            WRITE(3,*)'    LS2M MODEL      '
      WRITE(3,50)DESCR
      WRITE(3,*)' THESE TEST DATA ARE GENERATED FROM FOLLOWING
     1      PARAMETERS : '
      WRITE(3,60)TE0,TF0,TEI,TE1,TE2,TT1,TT2
```

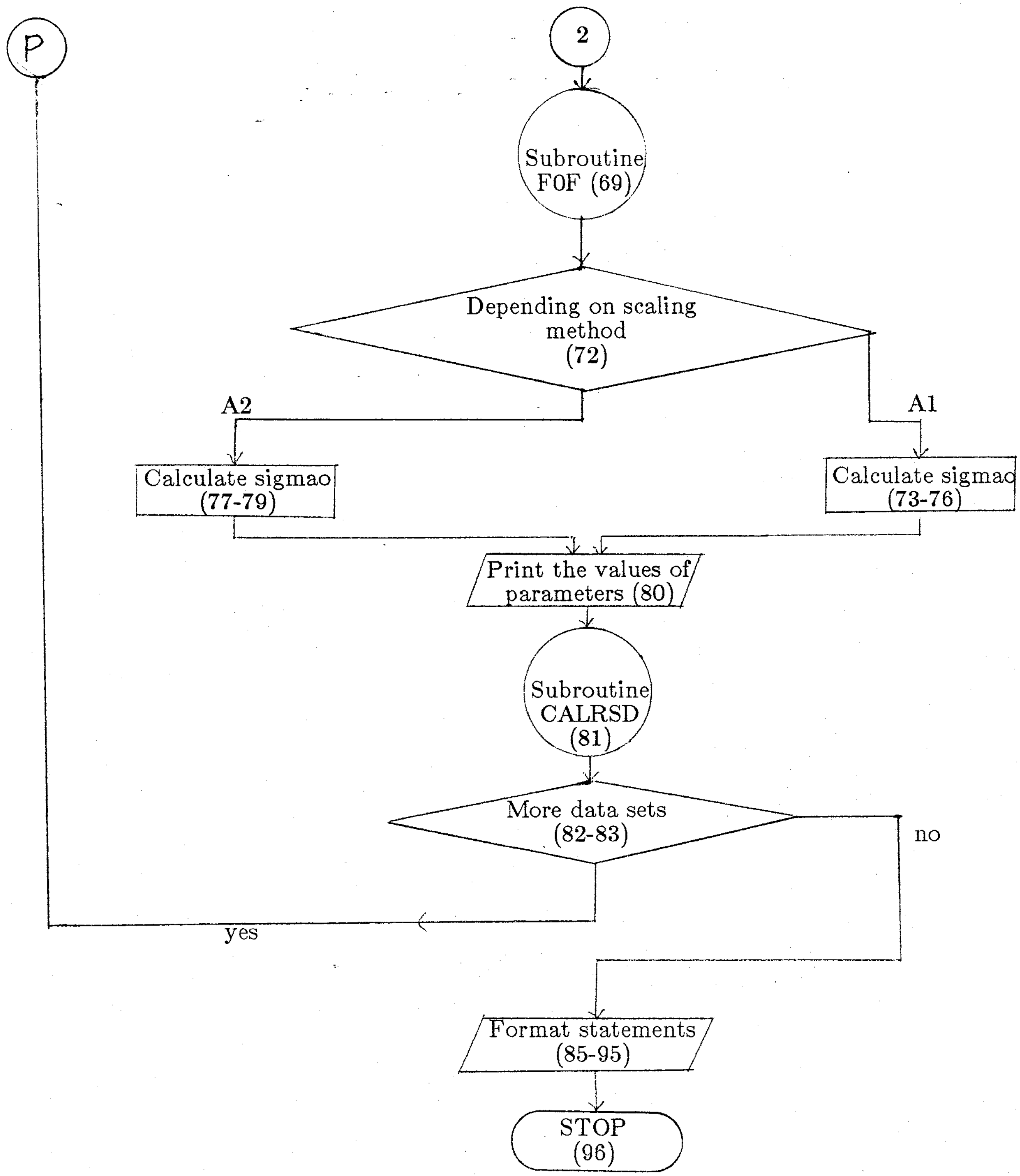
```
      EI=TEI
      ELSE
      READ(25,30)DESCR
      WRITE(3,*)'    LS2M MODEL    '
      WRITE(3,50)DESCR
      WRITE(5,*) ' Please input "EI" '
      READ(5,*)EI
      ENDIF

      READ(25,70) NDAT
      READ(25,80) (FD(I), XD(I), YD(I), I=1,NDAT)
      CLOSE(UNIT=25)

      TPI=6.2831853
      TPIK=TPI*1000.

      WRITE(5,*)' PLEASE INPUT STARTING POINT '
      READ(5,*)II
      WRITE(3,90)II

      SND = (NDAT - II)/MM+1
      SF2 = 0.;      SF4 = 0.

      WRITE(5,*)' Please input method for scaling the data, "A1" or "A2" '
      READ(5,30)SWITCH
      WRITE(5,95)SWITCH

      DO 100 I = II,NDAT,MM
      FF = FD(I)**2;      SF2 = SF2 + FF
  100 SF4 = SF4 + FF**2

      WRITE(3,105)

      CALL MIN

      CALL F0F

      TAU1=T1/TPIK
      TAU2=T2/TPIK

      IF (SWITCH .EQ. 'A1' ) THEN
      WRITE(5,*) ' A1 method need input geometrical factor "A/L" '
      WRITE(5,*) ' for calculating Sigma0 '
      READ(5,*) AL
      SIGMA0=TPIK*1.E-12*F0/AL
      ELSE
      SIGMA0=TPIK*F0*8.85E-14
      ENDIF
      WRITE(3,110) E0,F0,TAU1,E1,E2,TAU2,T1,T2,SIGMA0,B1,B2,EI,C1,C2
     1 ,F1,F2

      CALL CALRSD
      K=K+1
      IF(K.GE.NSET)STOP
```

```
      GO TO 10

20    FORMAT('1')
30    FORMAT(A)
40    FORMAT(7F)
50    FORMAT(A/)
60    FORMAT(/,7X,'E0 = ',F12.4,4X,'F0 = ',F12.4,4X,'EI = ',F12.4
     1,/7X,'E1 = ',F12.4,4X,'E2 = ',F12.4
     1,/7X,'T1 = ',F12.4,4X,'T2 = ',E12.4/)
70    FORMAT(I)
80    FORMAT(3F)
90    FORMAT(/2X,' STARTING POINT (CALCULATING RESIDUALS) : ', I3/)
95    FORMAT(/2X,'Scaling : Alternative ',2A)
105   FORMAT(/2X,'K',6X,'E0',10X,'E1',10X,'E2',11X,'C1',10X,'C2',
     1 10X,'SR',10X,'D'/)
110   FORMAT(/,7X,'E0 = ',F12.4,4X,'F0 = ',F12.4
     1,4X,'TAU1=',E12.4/7X,'E1 = ',F12.4,4X,'E2 = ',F12.4
     1,4X,'TAU2=',E12.4/7X,'T1 = ',F12.4,4X,'T2 = ',F12.4
     1,4X,'SIGMA0=',E12.4/7X,'B1 = ',F12.4,4X,'B2 = ',F12.4
     1,4X,'EI=',F12.4,/7X,'C1 = ',F12.4,4X,'C2 = ',F12.4/,7X,
     1 'F1 = ',F12.4,4X,'F2 = ',F12.4)
      STOP
      END
```

D7. LS2P flow sheet and listing

The flow diagram for LS2P




P
2
Subroutine
F0F (69)
Depending on scaling
method
(72)
A2
A1
Calculate sigmao
(77-79)
Calculate sigmao
(73-76)
Print the values of
parameters (80)
Subroutine
CALRSD
(81)
More data sets
(82-83)
no
yes
Format statements
(85-95)
STOP
(96)

LS2P program listing

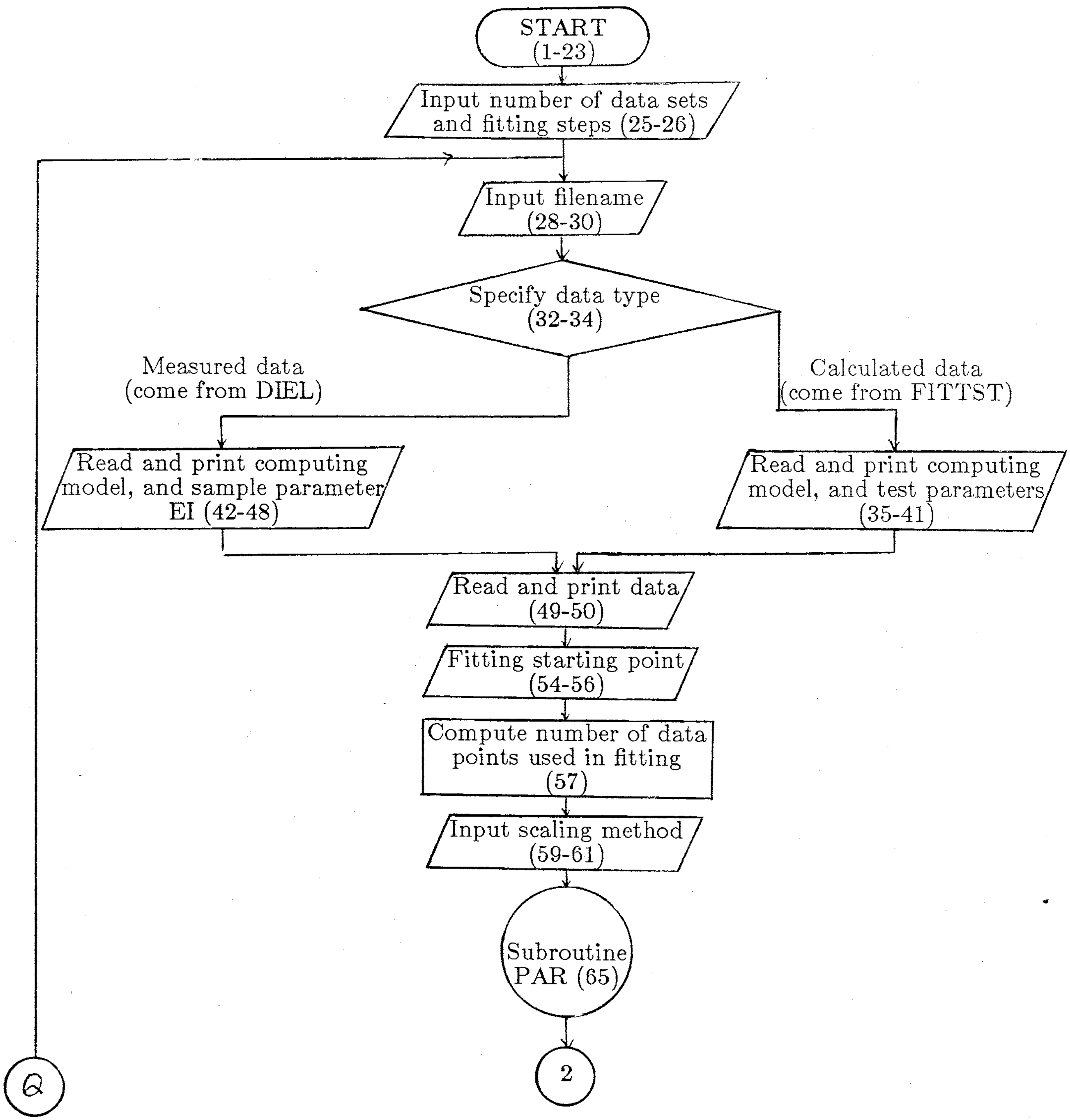
```
C     PROGRAM NAME : LS2P.FOR
C     Procedure to extract parameters F0, T, and Epsilon
C     E0, effective scaled value of driving capacitor.

C     Set of data containing frequencies [kHz],
C     real (XD), and imaginary (YD) components of the dielectric
C     spectrum.

C     Prior to inputting them into this program, XD and YD should be
C     scaled by one or other of two methods ;
C     Alternative 1 : Picofarads
C           X : Parallel capacitance
C           Y : Parallel conductance/omega

C     Alternative 2 : Nondimensional
C           X : Epsilon prime
C           Y : Epsilon double prime
C             Where :
C     OMEGA : 2*PI*FD(I),IN KILO RADIANS/SEC

C     Values for both scaling alternatives are directly taken
C     from output of DIEL.

      DOUBLE PRECISION DATIN,TEST
      CHARACTER*30 DESCR
      COMMON /A/NDAT,II,FD(30),XD(30),YD(30),SND,SF2,SF4,MM
      COMMON /C/E0,E02,EI,E1,T1,B1,C1,E2,T2,B2,C2,F0,SR,F1,F2
      COMMON/B/IS,IE

C     READ IN DATA INTO FD, XD, AND YD ARRAYS

      WRITE(5,*)' PLEASE INPUT NUMBER OF FILE SETS TO BE FITTED
     1 AND FITTING STEP '
      READ(5,*) NSET,MM
      WRITE(5,*)' PLEASE INPUT THE STARTING POINT AND ENDING POINT TO
     1 CALCULATE RESIDUALS FOR THE SECANT '
      READ(5,*)IS,IE
      K=0
   10 WRITE(5,*)' PLEASE INPUT FILE NAME '
      WRITE(3,20)
      READ(5,30)DATIN

      OPEN(UNIT=25,DEVICE='DSK',FILE=DATIN)

      WRITE(5,*)' Are these modelling data ? Type  YES  for " yes "
     1 & type  NO for " no " '

      READ(5,30)TEST
      IF(TEST.EQ.'YES')THEN
      READ(25,30)DESCR
      READ(25,40)TE0,TE1,TE2,TT1,TT2,TF0,TEI
```

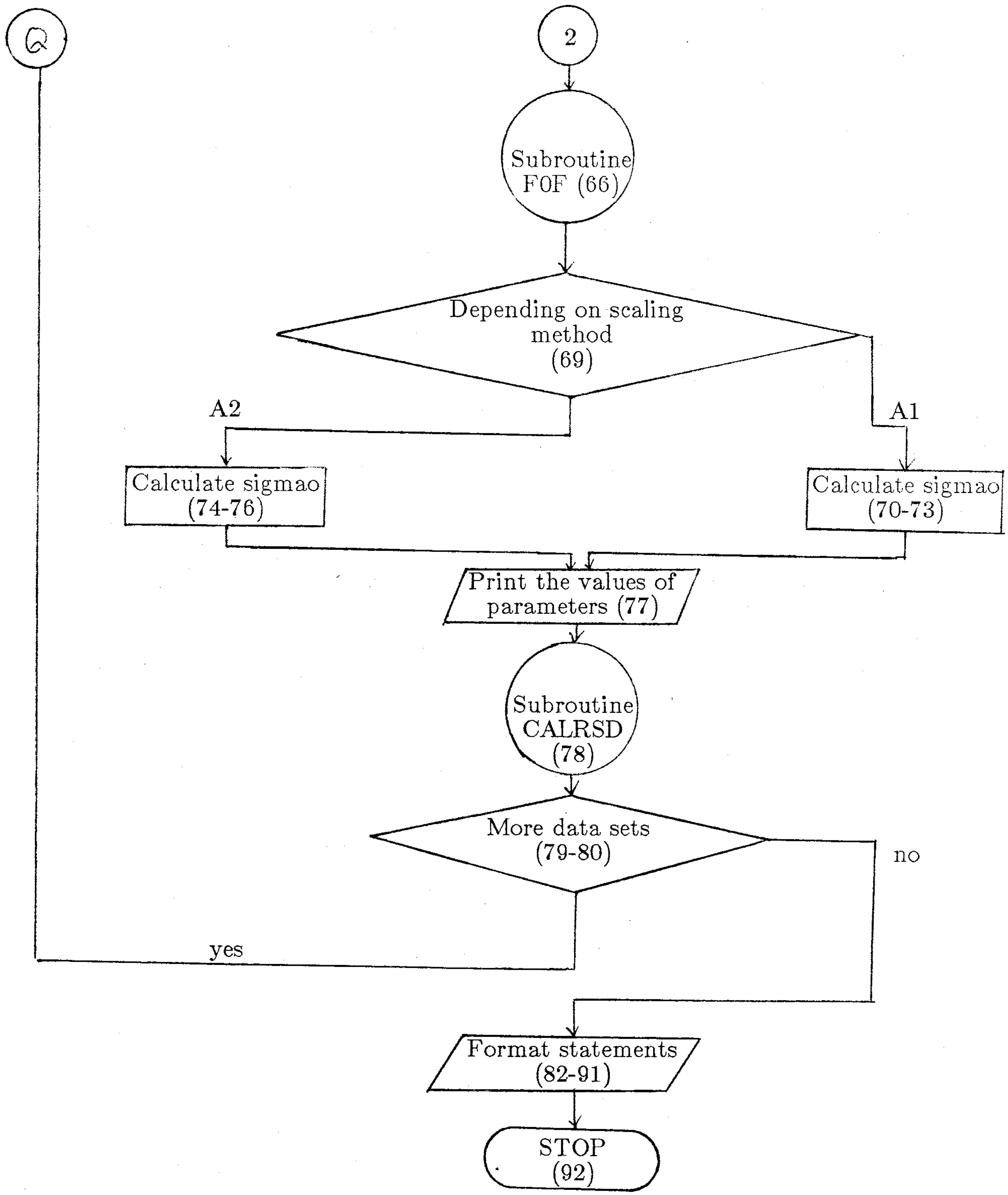
```
      WRITE(3,*)'     LS2P MODEL     '
      WRITE(3,50)DESCR
      WRITE(3,*)' THESE TEST DATA ARE GENERATED FROM FOLLOWING
     1      PARAMETERS : '
      WRITE(3,60)TE0,TF0,TEI,TE1,TE2,TT1,TT2
      EI=TEI
      ELSE
      READ(25,30)DESCR
      WRITE(3,*)'     LS2P MODEL     '
      WRITE(3,50)DESCR
      WRITE(5,*)' PLEASE INPUT "EI" '
      READ(5,*)EI
      ENDIF

      READ(25,70) NDAT
      READ(25,80) (FD(I), XD(I), YD(I),I=1,NDAT)

      CLOSE(UNIT=25)

      TPI=6.2831853
      TPIK=TPI*1000.

      WRITE(3,85)IS,IE
      WRITE(5,*)' PLEASE INPUT STARTING POINT '
      READ(5,*)II
      WRITE(3,90)II
      SND = (NDAT - II) / MM + 1

      SF2 = 0.;      SF4 = 0.

      WRITE(5,*)' Please input method for scaling the data, "A1" or "A2" '
      READ(5,30)SWITCH
      WRITE(3,95)SWITCH

      DO 100 I = II,NDAT,MM
      FF = FD(I)**2;      SF2 = SF2 + FF
  100 SF4 = SF4 + FF**2

      CALL SEC

      CALL F0F

      TAU1=T1 / TPIK
      TAU2=T2 / TPIK

      IF (SWITCH .EQ. 'A1' ) THEN
      WRITE(5,*) ' A1 method need input geometrical factor "A/L" '
      WRITE(5,*) ' for calculating the Sigma0 '
      READ(5,*) AL
      SIGMA0=TPIK*F0*1.0E-12/AL
      ELSE
      SIGMA0=TPIK*F0*8.85E-14
      ENDIF
      WRITE(3,110) E0,F0,TAU1,E1,E2,TAU2,T1,T2,SIGMA0,B1,B2,EI,C1
```

```
     1 ,C2,F1,F2
      CALL CALRSD
      K=K + 1
      IF(K.GE.NSET)STOP
      GO TO 100
20    FORMAT('1')
30    FORMAT(A)
40    FORMAT(7F)
50    FORMAT(A/)
60    FORMAT(/,7X,'E0 = ',F12.4,4X,'F0 = ',F12.4,4X,'EI = ',F12.4
     1,/7X,'E1 = ',F12.4,4X,'E2 = ',F12.4
     1,/7X,'T1 = ',F12.4,4X,'T2 = ',E12.4/)
70    FORMAT(I)
80    FORMAT(3F)
85    FORMAT(/2X,' E0 WAS DETERMINED BY SECANT METHOD USING POINT ',I2
     1 '-',I2/)
90    FORMAT(/2X,'FITTING STARTING POINT = ',I3/)
95    FORMAT(2X,'Scaling : Alternative ', 2A)
110   FORMAT(/,7X,'E0 = ',F12.6,4X,'F0 = ',F12.4
     1,4X,'TAU1=',E12.4/7X,'E1 = ',F12.4,4X,'E2 = ',F12.4
     1,4X,'TAU2=',E12.4/7X,'T1 = ',F12.4,4X,'T2 = ',F12.4
     1,4X,'SIGMA0=',E12.4/7X,'B1 = ',F12.4,4X,'B2 = ',F12.4
     1,4X,'EI=',F12.4,/7X,'C1 = ',F12.4,4X,'C2 = ',F12.4/,7X,
     1'F1 = ',F12.4,4X,'F2 = ',F12.4)
      STOP
      END
```

D8. LS2PQ flow sheet and listing

The flow diagram for LS2PQ




Q
2
Subroutine
FOF (66)
Depending on scaling
method
(69)
A2
A1
Calculate sigmao
(74-76)
Calculate sigmao
(70-73)
Print the values of
parameters (77)
Subroutine
CALRSD
(78)
More data sets
(79-80)
no
yes
Format statements
(82-91)
STOP
(92)

LS2PQ program listing

```
C     PROGRAM NAME : LS2PQ.FOR
C     This program computes a dielectric spectrum for measurements done
C     without a driving capacitor.

C     Procedure to extract parameters F0, T, and Epsilon
C     Set of data containing frequencies [kHz],
C     real (XD), and imaginary (YD) components of the dielectric
C     spectrum.

C     EI, high frequency permitivity

C     Prior to inputting them into this program, XD and YD should be
C     scaled by one or other of two methods ;
C     Alternative 1 : Picofarads
C              X : Parallel capacitance
C              Y : Parallel conductance/omega

C     Alternative 2 : Nondimensional
C           X : Epsilon prime
C           Y : Epsilon double prime
C       Where :
C     OMEGA : 2*PI*FD(I),IN KILO RADIANS/SEC

C     Values for both scaling alternatives are directly taken
C     from output of DIEL.

      DOUBLE PRECISION DATIN,TEST
      CHARACTER*30 DESCR
      COMMON /A/NDAT,II,FD(30),XD(30),YD(30),SND,SF2,SF4,MM,ID
      COMMON /C/EI,E1,T1,B1,C1,E2,T2,B2,C2,F0,SR,K,D,F1,F2

C     READ IN DATA INTO FD, XD, AND YD ARRAYS

      WRITE(5,*)' PLEASE INPUT NUMBER OF FILE SETS TO BE FITTED
     1 AND FITTING STEP'
      READ(5,*) NSET,MM
      K = 0
10    WRITE(5,*)' PLEASE INPUT FILE NAME '
      WRITE(3,20)
      READ(5,30)DATIN

      OPEN(UNIT=25,DEVICE='DSK',FILE=DATIN)

      WRITE(5,*)' Are these modelling data ? Type  YES  for " yes "
     & type  NO  for " no " '

      READ(5,30)TEST
      IF(TEST.EQ.'YES')THEN
      READ(25,30)DESCR
      READ(25,40)TE1,TE2,TT1,TT2,TF0,TEI
      WRITE(3,*)'    LS2PQ Model '
```

```
      WRITE(3,50)DESCR
      WRITE(3,*)' THESE TEST DATA ARE GENERATED FROM FOLLOWING
     1      PARAMETERS : '
      WRITE(3,60)TF0,TEI,TE1,TE2,TT1,TT2
      EI=TEI
      ELSE
      READ(25,30)DESCR
      WRITE(3,*)'     LS2PQ Model '
      WRITE(3,50)DESCR
      WRITE(5,*)' PLEASE INPUT "EI" '
      READ(5,*)EI
      ENDIF

      READ(25,70) NDAT
      READ(25,80) (FD(I), XD(I), YD(I), I=1,NDAT)

      CLOSE(UNIT=25)

      TPI = 6.2831853
      TPIK = TPI*1000.

      WRITE(5,*)' PLEASE INPUT FITTING STARTING POINT '
      READ(5,*)II
      WRITE(3,90)II
      SND = (NDAT - II)/MM + 1
      SF2 = 0.;       SF4 = 0.

      WRITE(5,*)' Please input method for scaling the data, "A1" or "A2" '
      READ(5,30)SWITCH
      WRITE(3,95)SWITCH

      DO 100 I = II,NDAT,MM
      FF = FD(I)**2;       SF2 = SF2 + FF
  100 SF4 = SF4 + FF**2

      CALL PAR

      CALL F0F

      TAU1 = T1/TPIK
      TAU2 = T2/TPIK

      IF (SWITCH .EQ. 'A1' ) THEN
      WRITE(5,*) ' A1 method need input geometrical factor "A/L" '
      WRITE(5,*) ' for calculating Sigma0 '
      READ(5,*) AL
      SIGMA0=TPIK*1.0E-12*F0/AL
      ELSE
      SIGMA0=TPIK*F0*8.85E-14
      ENDIF

      WRITE(3,110) F0,TAU1,E1,E2,TAU2,T1,T2,SIGMA0,B1,B2,EI,C1,C2
     1 ,F1,F2
```

```
      CALL CALRSD

      K = K + 1
      IF(K.GE.NSET)STOP
      GO TO 10

20    FORMAT('1')
30    FORMAT(A)
40    FORMAT(6F)
50    FORMAT(A/)
60    FORMAT(/7X,'F0 = ',F12.4,4X,'EI = ',F12.4
      1,/7X,'E1 = ',F12.4,4X,'E2 = ',F12.4
      1,/7X,'T1 = ',F12.4,4X,'T2 = ',E12.4/)
70    FORMAT(I)
80    FORMAT(3F)
90    FORMAT(/2X,'FITTING STARTING POINT = ',I3/)
95    FORMAT(2X,'Scaling : Alternative ', 2A)
110   FORMAT(/,7X,'F0 = ',F12.4
      1,4X,'TAU1=',E12.4/7X,'E1 = ',F12.4,4X,'E2 = ',F12.4
      1,4X,'TAU2=',E12.4/7X,'T1 = ',F12.4,4X,'T2 = ',F12.4
      1,4X,'SIGMA0=',E12.4/7X,'B1 = ',F12.4,4X,'B2 = ',F12.4
      1,4X,'EI=',F12.4,/7X,'C1 = ',F12.4,4X,'C2 = ',F12.4/7X,
      1 'F1 = ',F12.4,4X,'F2 = ',F12.4)
      STOP
      END


C     PAR subroutine
C     Computes dispersion parameters E1, E2, T1, T2
C     by least-squares fit between measured and computed
C     X, Y values at a number of measurement frequencies.

      SUBROUTINE PAR
      COMMON /A/NDAT,II,FD(30),XD(30),YD(30),SND,SF2,SF4,MM
      COMMON /C/EI,E1,T1,B1,C1,E2,T2,B2,C2,F0,SR,K,D,F1,F2
      DIMENSION A(4,4),G(4)

C     LEAST SQUARES SUMS

      SR = 0.;      SF2R = 0.;     SF4R = 0.;     SF6R = 0.
      SF2R2 = 0.;   SF4R2 = 0.;    SF6R2 = 0.;    SF8R2 = 0.

      DO 200 I = II,NDAT,MM
      F2 = FD(I)**2
      R = XD(I) - EI
      F2R = F2*R;                 F4R = F2*F2R
      F2R2 = F2R*R;               F4R2 = F4R*R
      F6R2 = F2*F4R2
      SR = SR + R;                SF2R = SF2R + F2R
      SF4R = SF4R + F4R;          SF6R = SF6R + F2*F4R
      SF2R2 = SF2R2 + F2R2;       SF4R2 = SF4R2 + F4R2
      SF6R2 = SF6R2 + F6R2
200   SF8R2 = SF8R2 + F2*F6R2
```

```
C     MATRIX COEFFICIENTS AND CONSTANTS

      A11 = SND; A12 = SF2; A13 = - SF2R; A14 = - SF4R; G1 = SR
      A21 = SF2; A22 = SF4; A23 = - SF4R; A24 = - SF6R; G2 = SF2R
      A31 = SF2R; A32 = SF4R; A33 = - SF4R2; A34 = - SF6R2; G3 = SF2R2
      A41 = SF4R; A42 = SF6R; A43 = - SF6R2; A44 = - SF8R2; G4 = SF4R2

C     SOLUTION FOR PARAMETERS

      A41 = A41/A44; A42 = A42/A44; A43 = A43/A44; G4 = G4/A44
      A11 = A11 - A14*A41;          A12 = A12 - A14*A42
      A13 = A13 - A14*A43;          G1 = G1 - A14*G4
      A21 = A21 - A24*A41;          A22 = A22 - A24*A42
      A23 = A23 - A24*A43;          G2 = G2 - A24*G4
      A31 = A31 - A34*A41;          A32 = A32 - A34*A42
      A33 = A33 - A34*A43;          G3 = G3 - A34*G4

      A31 = A31/A33;        A32 = A32/A33;        G3 = G3/A33
      A11 = A11 - A13*A31;  A12 = A12 - A13*A32;  G1 = G1 - A13*G3
      A21 = A21 - A23*A31;  A22 = A22 - A23*A32;  G2 = G2 - A23*G3
      A21 = A21/A22;                 G2 = G2/A22
      A11 = A11 - A12*A21;                G1 = (G1 - A12*G2)/A11

      G2 = G2 - A21*G1;     G3 = G3 - A31*G1;     G4 = G4 - A41*G1
      G3 = G3 - A32*G2;     G4 = G4 - A42*G2;     G4 = G4 - A43*G3
      G3H = G3*.5;              D = G3H**2 - G4
      IF(D.GT.0.) GO TO 220
      WRITE(3,210)
  210 FORMAT('0NEGATIVE DISCRIMINANT')
      E1 = G1;   C1 = G3H;    E2 = 0.;   C2 = 0.
      GO TO 230

  220 C1 = G3H + SQRT(D);        C2 = G3 - C1
      E2 = (G2 - C2*G1)/(C1 - C2);      E1 = G1 - E2

  230 T1 = SQRT(ABS(C1));        T2 = SQRT(ABS(C2))
      B1 = E1*T1;              B2 = E2*T2
      F1 = 1.0/T1;             F2 = 1.0/T2

      WRITE(3,240)
      WRITE(3,250)K, E0, E1, E2, C1, C2, SR,D
  240 FORMAT(/2X,'K',6X,'E0',10X,'E1',10X,'E2',11X,'C1',10X,'C2',
     1 10X,'SR',10X,'D'/)
  250 FORMAT(1DX,I2,F12.6,6(F12.4))
      RETURN
      END


C     F0F subroutine
C     Computes the dc conductance parameter from the
C     measurement-derived q-values and computed values E, T at each
C     frequency, then averages them for display as one value.

      SUBROUTINE F0F
```

```
      COMMON /A/NDAT,II,FD(30),XD(30),YD(30),SND,SF2,SF4,MM
      COMMON /C/EI,E1,T1,B1,C1,E2,T2,B2,C2,F0,SR,K,D

      S = 0.0

      DO 300 I = II,NDAT,MM
      F = FD(I);      FF = F**2
  300 S = S + YD(I)*FD(I) - (B1/(1.0+C1*FF)+B2/(1.0+C2*FF))*FF
      F0 = S/SND
      RETURN
      END


C     CALRSD subroutine
C     Computes residuals between "Calculated" and "Measured"
C     values, respectively, of X,Y,p,q, and fq, RMS deviations
C     of XY and fq.

      SUBROUTINE CALRSD
      COMMON /A/NDAT,II,FD(30),XD(30),YD(30),SND,SF2,SF4,MM,ID
      COMMON /C/EI,E1,T1,B1,C1,E2,T2,B2,C2,F0,SR,K,D,F1,F2
      DIMENSION PPP(30),QQQ(30),X(30),Y(30),PDAT(30),QDAT(30)

      SUMXY = 0.0
      SUMPQ = 0.0
      SUMFQ = 0.0

      WRITE(3,400)
      DO 430 J = 1,NDAT
      FF = FD(J)**2
      P = EI + E2 / (1.0+ C2 * FF) + E1 / (1.0 + C1 * FF)
      SQ = F0 + ( B2/(1.0 + C2 * FF) + B1/(1.0 + C1 * FF))* FF
      Q = SQ / FD(J)
      PPP(J) = P
      QQQ(J) = Q
      XXX = P
      YYY = Q
      RESX = XXX - XD(J)
      RESY = YYY - YD(J)
      DIFX = RESX/XXX*100.0
      DIFY = RESY/YYY*100.0
      XRMS = SQRT(( RESX**2 + RESY**2) / (XXX**2 + YYY**2))*100.0
      PDAT(J) = XD(J)
      QDAT(J) = YD(J)
      IF(J.LT.II) GO TO 410

      SUMXY = SUMXY + ABS(XRMS)
  410 WRITE(3,420)FD(J),XD(J),YD(J),XXX,YYY,RESX,RESY,DIFX,DIFY,XRMS
  430 CONTINUE
      XYAVE = SUMXY / SND
      WRITE(3,440)XYAVE

      WRITE(3,450)
      DO 470 J = 1,NDAT
```

```
      RESP = PPP(J) - PDAT(J)
      RESQ = QQQ(J) - QDAT(J)
      DIFP = RESP/PPP(J)*100.0
      DIFQ = RESQ/QQQ(J)*100.0
      PRMS = SQRT(( RESP**2 + RESQ**2)/( PDAT(J)**2 + QDAT(J)**2))*100.0
      IF(J.LT.II) GO TO 460

      SUMPQ = SUMPQ + ABS(PRMS)
460   WRITE(3,420)FD(J),PDAT(J),QDAT(J),PPP(J),QQQ(J),RESP,RESQ,DIFP
     1 ,DIFQ,PRMS
470   CONTINUE
      PQAVE = SUMPQ / SND
      WRITE(3,440)PQAVE

      WRITE(3,480)
      DO 510 J = 1,NDAT
      FF = FD(J)**2
      FQDAT = FD(J) * QDAT(J)
      DIF = FQDAT - ( B1/(1. + C1 * FF ) + B2/(1. + C2 * FF)) * FF
      FQ = FD(J) * QQQ(J)
      RESFQ = FQ - FQDAT
      FQRMS = RESFQ / FQDAT*100.0

      IF(J.LT.II) GO TO 490
      SUMFQ = SUMFQ + ABS(FQRMS)
490   WRITE(3,500)FD(J),FQDAT,FQ,RESFQ,FQRMS,DIF
510   CONTINUE
      FQAVE = SUMFQ / SND
      WRITE(3,520)FQAVE

400   FORMAT(//,T21,'MEASURED',T39,'CALCULATED',T60,'RESIDUALS',T79,
     1 '% DIFFERENCE',T97,'RMSXY',/T21,'--------',T39,'----------'
     1 ,T60,'---------',T79,'------------',T97,'-----',/1X,
     1 'FREQ. (K HZ)',T19,'X',T28,'Y',T38,'X',T48,'Y',T58,'X',T68,
     1 'Y',T78,'X',T88,'Y')
420   FORMAT(1X,F10.5,2F10.2,7F10.3)
440   FORMAT(/T92,F10.3//)
450   FORMAT('1',/,1X,'PAGE : 2 ',//,T21,'MEASURED',T39,'CALCULATED',
     1 T60,'RESIDUALS',T79,'% DIFFERENCE',T97,'RMSPQ',/T21,'--------',
     1 T39,'----------',T60,'---------',T79,'------------',T97,'-----',
     1 /1X,'FREQ. (K HZ)',T19,'P',T28,'Q',T38,'P',T49,'Q',T58,'P',T68,
     1 'Q',T78,'P',T88,'Q')
480   FORMAT(//,T21,'MEASURED',T39,'CALCULATED',T60,'RESIDUALS',T79,
     1 '% DIFFERENCE',T97,'F0',/T21,'--------',T39,'----------'
     1 ,T60,'---------',T79,'------------',T97,'--',/1X,
     1 'FREQ. (K HZ)',T23,'FQ',T43,'FQ',T63,'FQ',T83,'FQ')
500   FORMAT(1X,F10.3,5X,F10.3,10X,F10.3,10X,F10.3,10X,F10.3,5X,F10.3)
520   FORMAT(/T77,F10.3//)
      RETURN
      END
```

Appendix E : Point-Fitting Programs

E1. Introduction

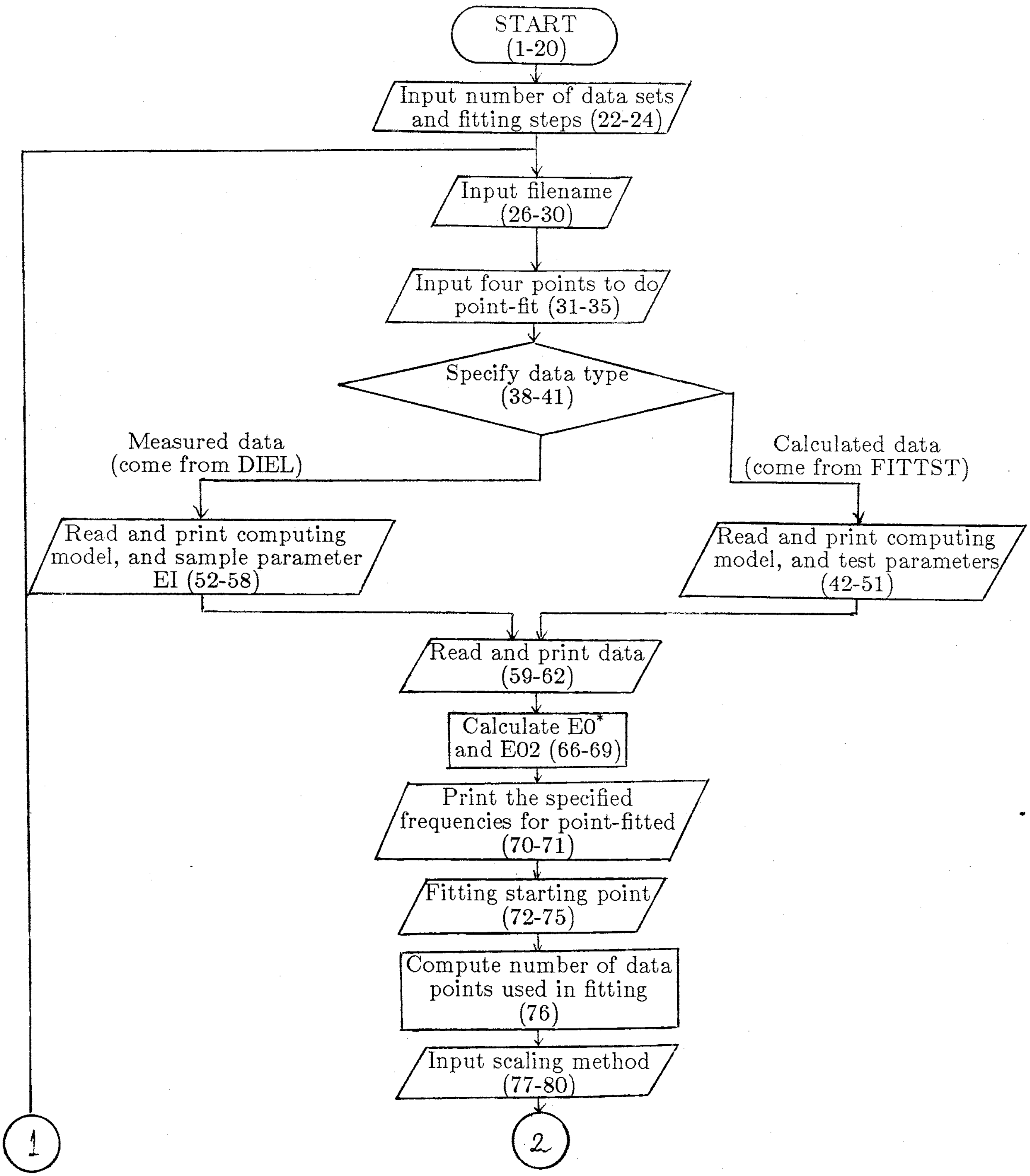
Programs whose designation begins with letters PF (Table VI) compute dispersion parameters from a number of equations equal to the number of Debye dispersion parameters (i.e. 2 equations per Debye element). This is done in subroutine PAR (Appendix C4), where the development is discussed.

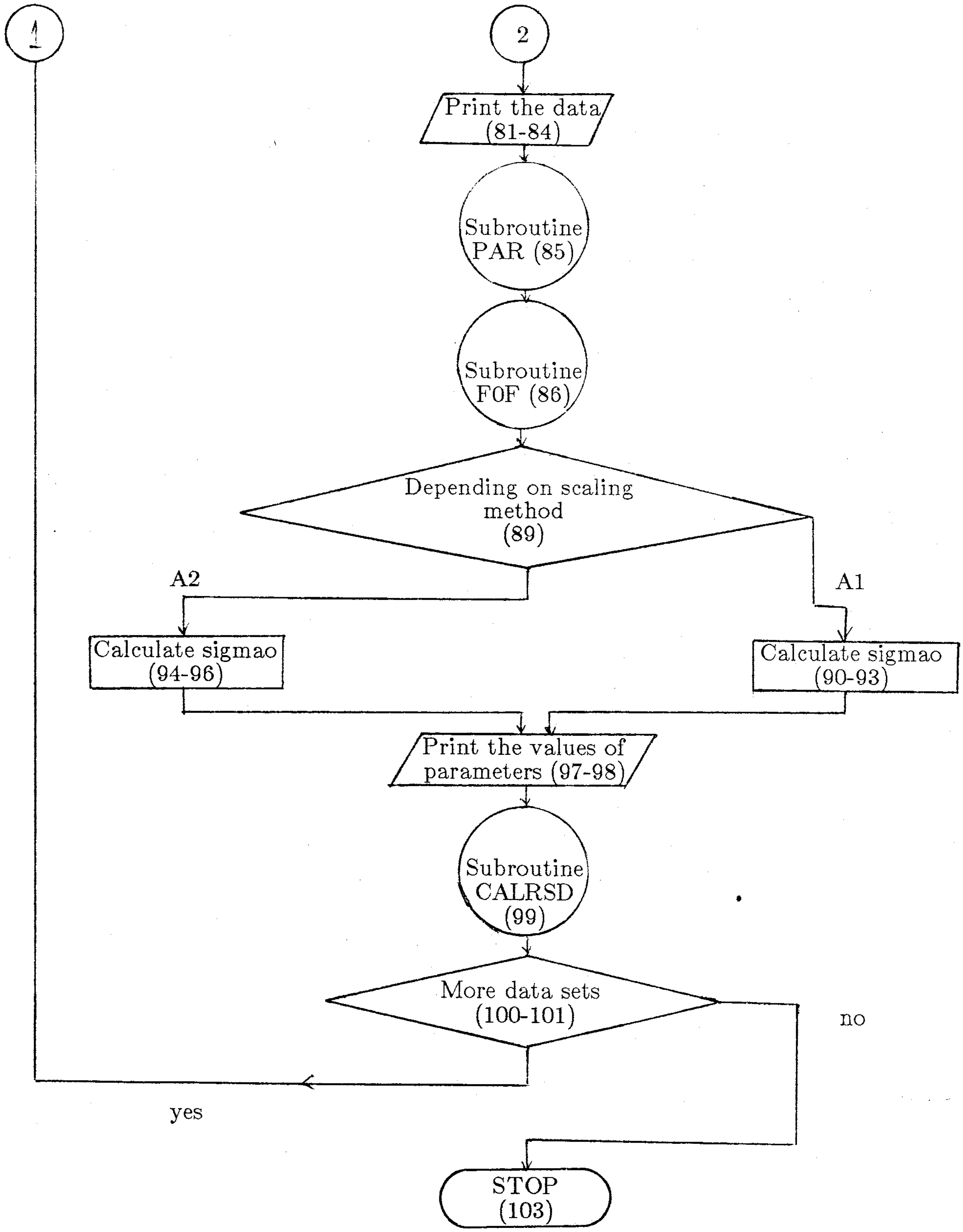
In all other respects these programs are identical to the least-squares fitting programs described in Appendix D. The list of programs is as follows :

1. PF2X2 : Fitting program for data with two Debye elements (where E0 is extrapolated from the first two data points).
2. PF2X3 : Fitting program for data with two Debye elements (where E0 is extrapolated from the first three data points).
3. PF2X4 : Fitting program for data with two Debye elements (where E0 is extrapolated from the first four data points).
4. PF2F : Fitting program for data with two Debye elements (where E0 is fixed).
5. PF2M : Fitting program for data with two Debye elements (where E0 is found by minimizing sum of residuals).
6. PF2P : Fitting program for data with two Debye elements (where E0 is found by a secant method).
7. PF2PQ : Fitting program for data with two Debye elements (where E0 is zero; i.e. no blocking layers used).

E2. PF2X2 flow sheet and listing

The flow diagram for PF2X2





* E0 evaluation : PF2X3 uses a 3-point extrapolation. Substitute statements 66-68 by 366-373. PF2X4 uses a 4-point extrapolation. Substitute statements 66-68 by 466-485. PF2F uses a fixed and pre-determined value of E0. Substitute statements 66-68 by 566-568.

PF2X2 program listing

```
C     PROGRAM : PF2X2.FOR
C     Procedure to extract parameters F0, T and Epsilon
C     E0, effective scaled value of driving capacitor.

C     Set of data containing frequencies [kHz],
C     real (XD), and imaginary (YD) components
C     of the complex dielectric spectrum.

C     Prior to inputting them into this program, XD and YD
C     should be scaled by one or other of two methods :
C     Alternative 1 : Picofarads
C     X : Parallel capacitance
C     Y : Parallel conductance/omega

C     Alternative 2 : Nondimensional
C     X : Epsilon 1
C     Y : Epsilon 2

C     Values for both scaling alternatives are directly taken from
C     output of DIEL

      CHARACTER*30 DESCR
      CHARACTER*12 DATIN
      COMMON /A/NDAT,II,FD(30),XD(30),YD(30),SND,R3,R4,IPA(4),MM
      COMMON /C/E0,E02,EI,E1,T1,B1,C1,E2,T2,B2,C2,F0,SR,F1,F2

C     READ IN DATA INTO FD, XD, AND YD ARRAYS

      WRITE(5,*) ' Please input number of file sets to be fitted'
      WRITE(5,*) ' and fitting step '
      READ(5,*)NSET,MM
      K=0
10    WRITE(5,*)' PLEASE INPUT THE FILE NAME '
      WRITE(3,20)
20    FORMAT('1')
      READ(5,30)DATIN
30    FORMAT(A)
      WRITE(5,*)' PLEASE INPUT ORDER NUMBERS CORRESPONDING TO '
      WRITE(5,*)' FOUR FREQUENCIES YOU HAVE SELECTED FOR POINT FIT '
      READ(5,*)N1,N2,N3,N4
      IPA(1)= N1 ; IPA(2)= N2
      IPA(3)= N3 ; IPA(4)= N4

      OPEN(UNIT=1,DEVICE='DSK',FILE=DATIN)

C     Check the data type

      WRITE(5,*) ' Are these model data ? Type YES for'
      WRITE(5,*) ' "model data" Type NO for "measured data" '

      READ(5,30)TEST
```

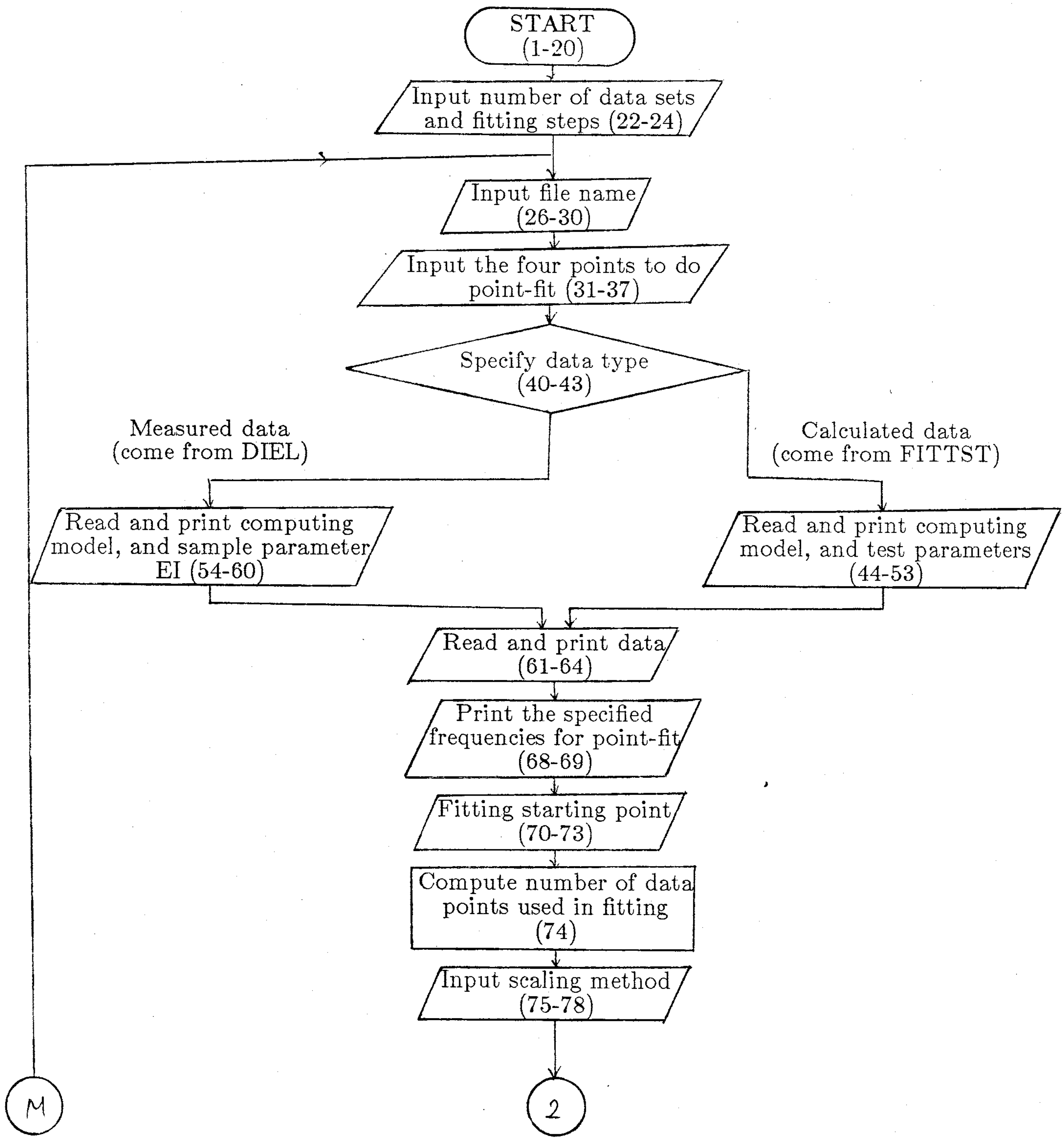
```
      IF(TEST.EQ.'YES')THEN
      READ(1,30)DESCR
      READ(1,40)TE0,TE1,TE2,TT1,TT2,TF0,TEI
40    FORMAT(1X,7F)
      WRITE(3,*)'   PF2X [2-PONT] MODEL  '
      WRITE(3,50)DESCR
50    FORMAT(A/)
      WRITE(3,*)' THESE TEST DATA ARE GENERATED FROM FOLLOWING
      1     PARAMETERS : '
      WRITE(3,60)TE0,TF0,TEI,TE1,TE2,TT1,TT2
60    FORMAT(/,7X,'E0 = ',F12.4,4X,'F0 = ',F12.4,4X,'EI = '
      1     ,F12.4,/7X,'E1 = ',F12.4,4X,'E2 = ',F12.4,/7X,'T1 = '
      1     ,F12.4,4X,'T2 = ',E12.4/)
      EI=TEI
      ELSE
      READ(1,30)DESCR
      WRITE(3,*)'   PF2X [2-POINT] MODEL     '
      WRITE(3,50)DESCR
      WRITE(5,*)' PLEASE INPUT "EI" '
      READ(5,*)EI
      ENDIF

      READ(1,70)NDAT
70    FORMAT(I)
      READ(1,80) (FD(I),XD(I),YD(I), I=1,NDAT)
80    FORMAT(F,F,F)

      CLOSE(UNIT=1)

      TPI=6.2831853
      TPIK=TPI*1000.

C     Using 2-point extrapolation evaluate E0

      X1 = XD(1)          ;    X2 = XD(2)
      E0=X1+(X1-X2)/(X2/X1*(FD(2)/FD(1))**2-1.0)
      E02 = E0**2

      WRITE(3,85)FD(N1),FD(N2),FD(N3),FD(N4)
85    FORMAT(1X,'FIT P FOR RELAXATION COEFFICIENTS USING ',4(F8.5,2X)
      1 ,'KHZ')
      WRITE(5,*)' PLEASE INPUT STARTING POINT '
      READ(5,*) II
      WRITE(3,90)II
90    FORMAT(/2X,'FITTING STARTING POINT = ',I3/)
      SND=(NDAT-II)/MM+1

      WRITE(5,*)' Please input method for scaling the data,
      1 "A1" or "A2" '
      READ(5,30)SWITCH
      WRITE(3,95)SWITCH
95    FORMAT(2X,'Scaling : Alternative ', 2A)

      WRITE(3,96)
```

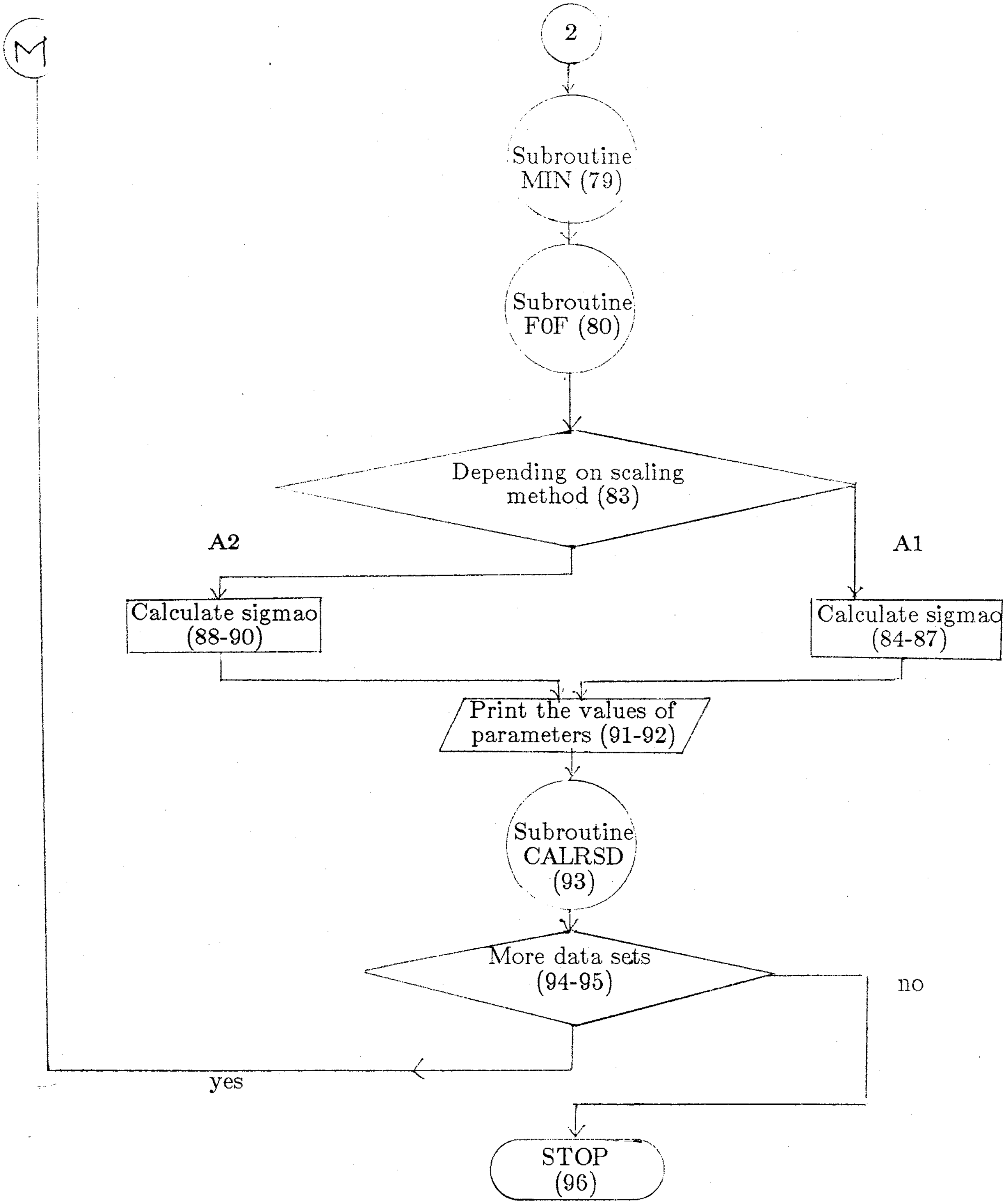
```
96   FORMAT(/,7X,'DATA',/,5X,'FREQ.(KHERTZ)',12X,'X',15X,'Y')
     WRITE(3,97) (I,FD(I),XD(I),YD(I), I=1,NDAT)
97   FORMAT(2X,I2,1X,F,3X,F,3X,F)

     CALL PAR

     CALL F0F

     TAU1=T1/TPIK
     TAU2=T2/TPIK

     IF (SWITCH .EQ. 'A1') THEN
     WRITE(5,*)' A1 method need input geometrical factor "A/L" '
     WRITE(5,*)' for calculating SIGMA0 '
     READ(5,*) AL
     SIGMA0=TPIK*1.0E-12*F0/AL
     ELSE
     SIGMA0=TPIK*F0*8.85E-14
     ENDIF
     WRITE(3,110) E0,F0,TAU1,E1,E2,TAU2,T1,T2,SIGMA0,C1,C2,EI,
     1 F1,F2
110  FORMAT(/,7X,'E0 = ',F12.4,4X,'F0 = ',F12.4,4X,'TAU1= ',E12.4
     1,/7X,'E1 = ',F12.4,4X,'E2 = ',F12.4,4X,'TAU2=',E12.4
     1,/7X,'T1 = ',F12.4,4X,'T2 = ',F12.4,4X,'SIGMA0=',E12.4
     1,/7X,'C1 = ',F12.4,4X,'C2 = ',F12.4,4X,'EI = ',F12.4
     1,/7X,'F1 = ',F12.4,4X,'F2 = ',F12.4)

     CALL CALRSD

     K = K + 1
     IF (K .GE. NSET) STOP
     GO TO 10
     STOP
     END
```

```
C     Using 3-point extrapolation evaluate E0

      A12 = FD(1)**2   ;  X1 = XD(1)   ;  A13 = X1*A12
      A22 = FD(2)**2   ;  X2 = XD(2)   ;  A23 = X2*A22
      A32 = FD(3)**2   ;  X3 = XD(3)   ;  A33 = X3*A32

      A31 = 1. / A33   ; A32 = A32 / A33  ; X3 = X3 / A33
      A11 = 1. - A13*A31; A12 = A12 - A13*A32  ;  X1 = X1 - A13*X3
      A21 = 1. - A23*A31  ; A22 = A22 - A23*A32  ; X2 = X2 - A23*X3

      E0 = (A22*X1 - A12*X2) / (A11*A22 - A12*A21)


C     Using 4-point extrapolation evaluate the E0

      I = 1       ; FF1 = FD(I)**2    ; X1 = XD(I)
      I = I + 1   ; FF2 = FD(I)**2    ; X2 = XD(I)
      I = I + 1   ; FF3 = FD(I)**2    ; X3 = XD(I)
      I = I + 1   ; FF4 = FD(I)**2    ; X4 = XD(I)

      A12 = FF1  ;  A13 = FF1*X1 ; A14 = FF1*A13 ; R1 = X1
      A22 = FF2  ;  A23 = FF2*X2 ; A24 = FF2*A23 ; R2 = X2
      A32 = FF3  ;  A33 = FF3*X3 ; A34 = FF3*A33 ; R3 = X3
      A42 = FF4  ;  A43 = FF4*X4 ; A44 = FF4*A43 ; R4 = X4

      A41 = 1.0/A44 ; A42 = A42/A44 ;  A43 = A43/A44  ; R4 = R4/A44
      A11 = 1.0 - A14*A41        ;  A12 = A12 - A14*A42
      A13 = A13 - A14*A43        ;  R1 = R1 - A14*R4

      A21 = 1.0 - A24*A41        ;  A22 = A22 - A24*A42
      A23 = A23 - A24*A43        ;  R2 = R2 - A24*R4

      A31 = 1.0 - A34*A41        ;  A32 = A32 - A34*A42
      A33 = A33 - A34*A43        ;  R3 = R3 - A34*R4

      A31 = A31/A33     ; A32 = A32/A33       ;  R3 = R3/A33
      A11 = A11 - A13*A31 ; A12 = A12 - A13*A32  ;  R1 = R1 - A13*R3
      A21 = A21 - A23*A31 ; A22 = A22 - A23*A32  ;  R2 = R2 - A23*R3

      E0 = (R1*A22 - R2*A12)/(A11*A22 - A12*A21)


C     FIXED E0

      WRITE(5,*)' INPUT E0 = ? '
      READ(5,*)E0
```

E3. PF2M flow sheet and listing

The flow diagram for PF2M




M
2
Subroutine MIN (79)
Subroutine F0F (80)
Depending on scaling method (83)
A2
A1
Calculate sigmao (88-90)
Calculate sigmao (84-87)
Print the values of parameters (91-92)
Subroutine CALRSD (93)
More data sets (94-95)
no
yes
STOP (96)

PF2M program listing

```
C     Program PF2M.FOR
C     PROCEDURE TO EXTRACT THE PARAMETERS F0,T and Epsilon
C     E0, effective scaled dielectric constant of driving capacitor.

C     Set of data containing frequencies (kHz),
C     real (XD) and imaginary (YD) components of the dielectric
C     spectrum.
C     Prior to inputting them into this program, XD and YD
C     should be scaled by one or other of two methods :
C     Alternative 1 : Picofarads
C            X : Parallel capacitance
C            Y : Parallel conductance/omega

C     Alternative 2 : Nondimensional
C            X : Epsilon 1
C            Y : Epsilon 2

C     Values for both scaling alternatives are directly taken from
C     output of DIEL.

      CHARACTER*30 DESCR
      CHARACTER*12 DATIN
      COMMON /A/NDAT,II,FD(30),XD(30),YD(30),SND,R3,R4,IPA(4),MM
      COMMON /C/E0,E02,EI,E1,T1,B1,C1,E2,T2,B2,C2,F0,SR,F1,F2

C     READ IN DATA INTO FD, XD, AND YD ARRAYS

      WRITE(5,*) ' Please input number of file sets to be fitted'
      WRITE(5,*) ' and fitting step '
      READ(5,*)NSET,MM
      KK=0
10    WRITE(5,*)' PLEASE INPUT THE FILE NAME '
      WRITE(3,20)
20    FORMAT('1')
      READ(5,30)DATIN
30    FORMAT(A)
      WRITE(5,35)
35    FORMAT(1X, 'PLEASE INPUT ORDER NUMBERS CORRESPONDING TO')
      WRITE(5,36)
36    FORMAT(1X,' FOUR FREQUENCIES YOU HAVE SELECTED FOR POINT FIT')
      READ(5,*)N1,N2,N3,N4
      IPA(1)= N1 ; IPA(2)= N2
      IPA(3)= N3 ; IPA(4)= N4

      OPEN(UNIT=1,DEVICE='DSK',FILE=DATIN)

C     Check the data type

      WRITE(5,*) ' Are these model data ? Type YES for'
      WRITE(5,*) ' "model data" Type NO for "measured data" '
      READ(5,30)TEST
```

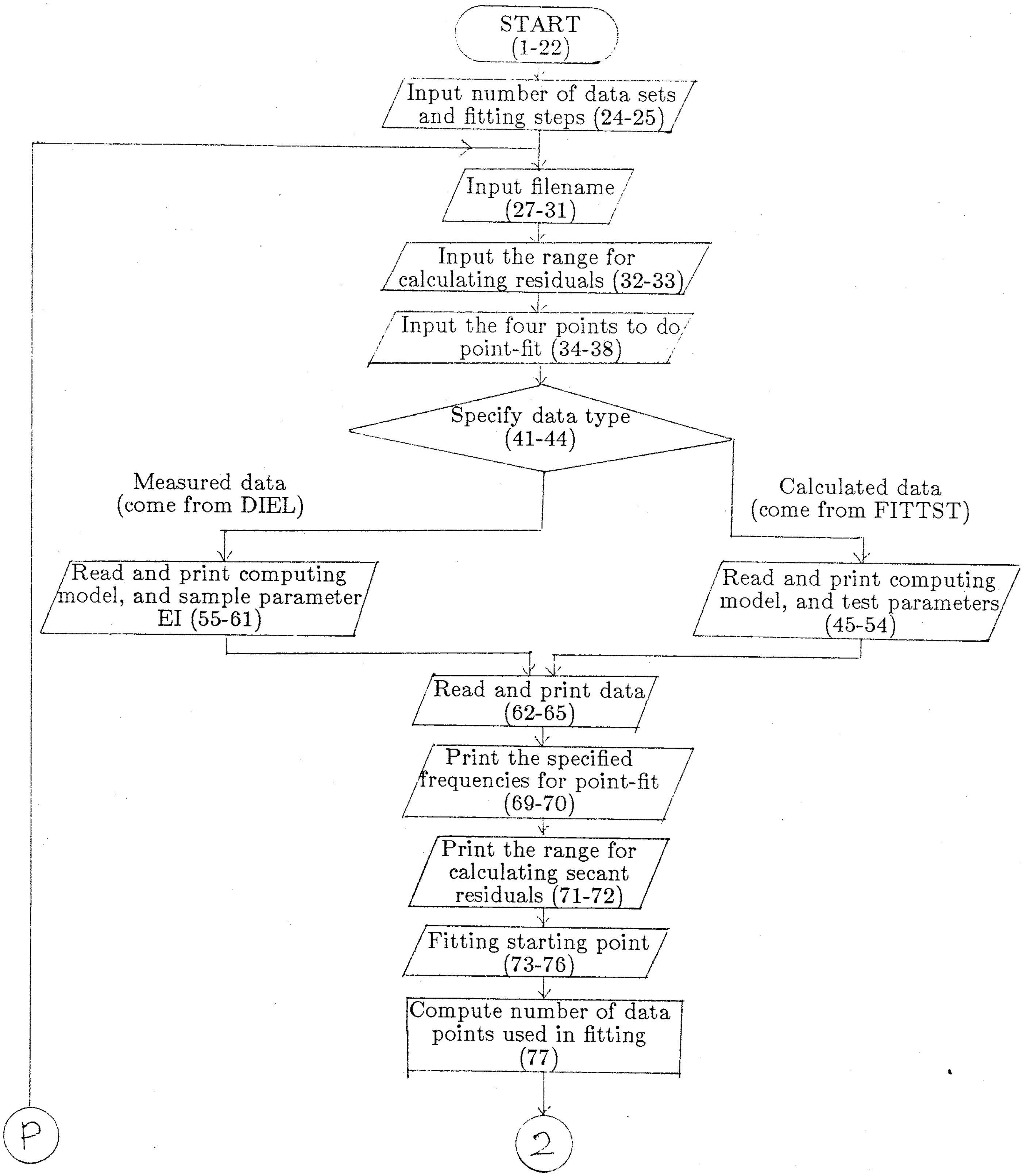
```
      IF(TEST.EQ.'YES')THEN
      READ(1,30)DESCR
      READ(1,40)TE0,TE1,TE2,TT1,TT2,TF0,TEI
40    FORMAT(1X,7F)
      WRITE(3,*)'   PF2M MODEL    '
      WRITE(3,50)DESCR
50    FORMAT(A/)
      WRITE(3,*)' THESE TEST DATA ARE GENERATED FROM FOLLOWING
      1     PARAMETERS : '
      WRITE(3,60)TE0,TF0,TEI,TE1,TE2,TT1,TT2
60    FORMAT(/,7X,'E0 = ',F12.4,4X,'F0 = ',F12.4,4X,'EI = '
      1       ,F12.4,/7X,'E1 = ',F12.4,4X,'E2 = ',F12.4,/7X,'T1 = '
      1       ,F12.4,4X,'T2 = ',E12.4/)
      EI=TEI
      ELSE
      READ(1,30)DESCR
      WRITE(3,*)'   PF2M MODEL    '
      WRITE(3,50)DESCR
      WRITE(5,*)' PLEASE INPUT "EI" '
      READ(5,*)EI
      ENDIF

      READ(1,70)NDAT
70    FORMAT(I)
      READ(1,80) (FD(I),XD(I),YD(I), I=1,NDAT)
80    FORMAT(F,F,F)

      CLOSE(UNIT=1)

      TPI=6.2831853
      TPIK=TPI*1000.

      WRITE(3,85)FD(N1),FD(N2),FD(N3),FD(N4)
85    FORMAT(1X,'FIT P FOR RELAXATION COEFFICIENTS USING ',4(F8.5,2X)
      1 ,'KHZ')
      WRITE(5,*)' PLEASE INPUT STARTING POINT '
      READ(5,*) II
      WRITE(3,90)II
90    FORMAT(/2X,'FITTING STARTING POINT = ',I3/)
      SND=(NDAT-II)/MM+1

      WRITE(5,*)' Please input method for scaling the data,
      1 "A1" or "A2" '
      READ(5,30)SWITCH
      WRITE(3,95)SWITCH
95    FORMAT(2X,'Scaling : Alternative ', 2A)

      CALL MIN

      CALL F0F

      TAU1=T1/TPIK
      TAU2=T2/TPIK
```

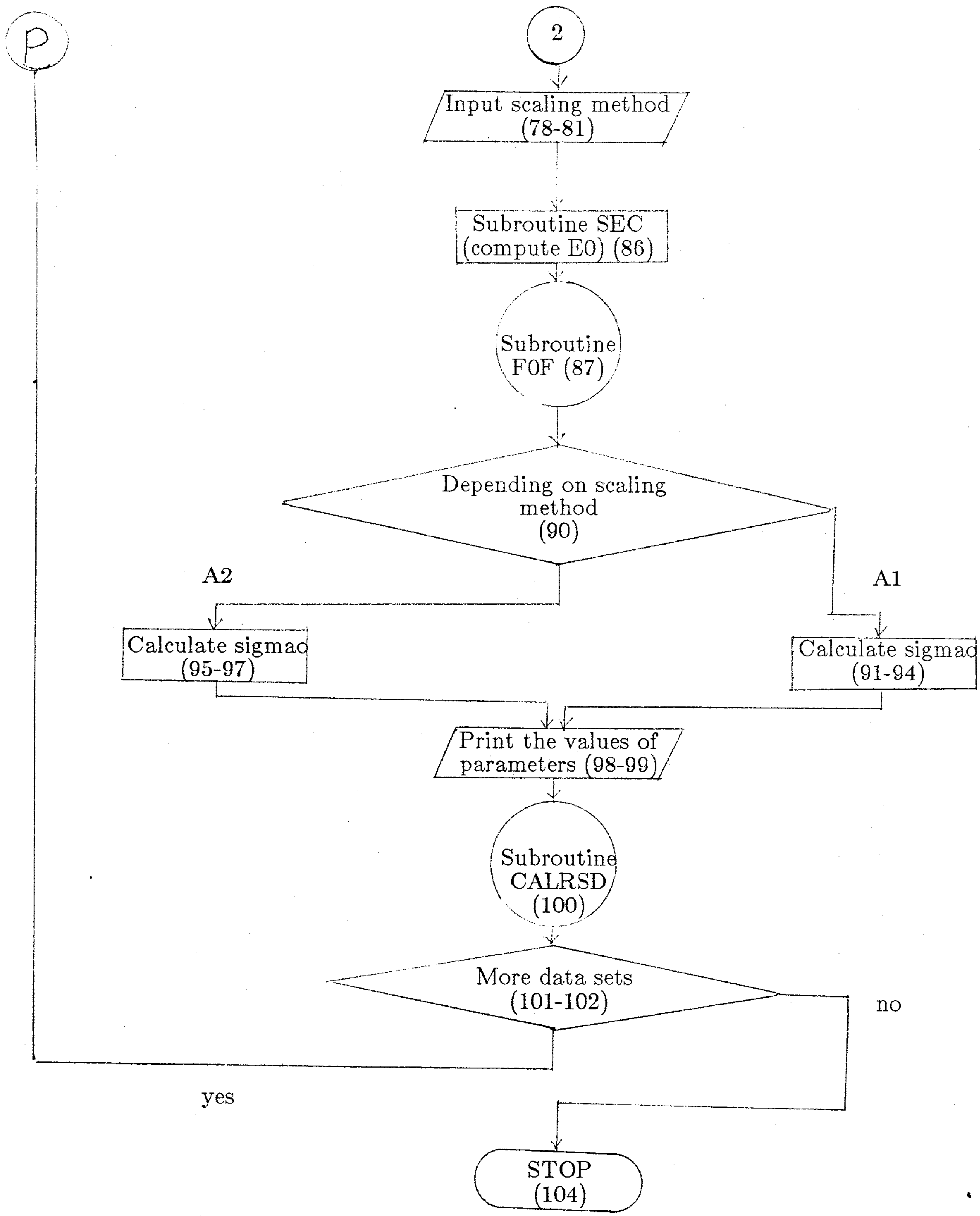
```
      IF (SWITCH .EQ. 'A1') THEN
      WRITE(5,*)' A1 method need input geometrical factor "A/L" '
      WRITE(5,*)' for calculating SIGMA0 '
      READ(5,*) AL
      SIGMA0=TPIK*1.0E-12*F0/AL
      ELSE
      SIGMA0=TPIK*F0*8.85E-14
      ENDIF
      WRITE(3,110) E0,F0,TAU1,E1,E2,TAU2,T1,T2,SIGMA0,C1,C2,EI,
     1 F1,F2
110   FORMAT(/,7X,'E0 = ',F12.4,4X,'F0 = ',F12.4,4X,'TAU1= ',E12.4
     1,/7X,'E1 = ',F12.4,4X,'E2 = ',F12.4,4X,'TAU2=',E12.4
     1,/7X,'T1 = ',F12.4,4X,'T2 = ',F12.4,4X,'SIGMA0=',E12.4
     1,/7X,'C1 = ',F12.4,4X,'C2 = ',F12.4,4X,'EI = ',F12.4
     1,/7X,'F1 = ',F12.4,4X,'F2 = ',F12.4)

      CALL CALRSD

      KK = KK + 1
      IF (KK .LT. NSET ) GO TO 10
      STOP
      END


C     MIN subroutine
C     This subroutine computes an E0 value by minimiing the sums of
C     deviations between measured X, Y values and those derived with E0
C     values deviating systematically from an initially assumed value.

      SUBROUTINE MIN
      COMMON /A/NDAT,II,FD(30),XD(30),YD(30),SND,R3,R4,IPA(4),MM
      COMMON /C/E0,E02,EI,E1,T1,B1,C1,E2,T2,B2,C2,F0,SR,F1,F2
      X1 = XD(1)
      D = (X1 - XD(2))/((FD(2)/FD(1))**2 - 1.)
      X2 = X1 + D;   E0 = X2;   CALL PAR;   S2 = SR

      IF(D.LT.1.) D = 1.

      X1 = X2 - D;   E0 = X1;   CALL PAR;   S1 = SR

10    IF(S2.LT.S1) GO TO 4

      X3 = X2;       S3 = S2;   X2 = X1;    S2 = S1
      X1 = X1 - D;   E0 = X1;   CALL PAR;   S1 = SR
      GO TO 8

4     X3 = X2 + D;   E0 = X3;   CALL PAR;   S3 = SR

8     TS = (S1 + S3)*.5 - S2
      Z = - (S3 - S1)*D*.25/TS
      X4 = X2 + Z;   E0 = X4;   CALL PAR;   S4 = SR

      DD = D**2;                ZZ = Z**2
      C = TS/DD;                T1 = (S3 - S1)/(D + D)
```

```
T4 = (S4 - S2 - ZZ*C)/Z;    G = (T1 - T4)/(DD - ZZ)
B = T4 - ZZ*G

RR=3.*B*G/C**2
IF (RR.GT.1)RR=1.0
X5 = X2 - B/(C*(1. + SQRT(1. - RR)))
E0 = X5;                  CALL PAR;    S5 = SR

Q4 = (S4 - S2)/(X4 - X2);   Q5 = (S5 - S2)/(X5 - X2)
C = (Q5 - Q4)/(X5 - X4);    B = Q5 - (X5 - X2)*C
X6 = X2 - .5*B/C;           E0 = X6;     CALL PAR

RETURN
END
```

E4. PF2P flow sheet and listing

The flow diagram for PF2P




P
2
Input scaling method (78-81)
Subroutine SEC (compute E0) (86)
Subroutine F0F (87)
Depending on scaling method (90)
A2
A1
Calculate sigmac (95-97)
Calculate sigmac (91-94)
Print the values of parameters (98-99)
Subroutine CALRSD (100)
More data sets (101-102)
no
yes
STOP (104)

PF2P program listing

```
C    PROGRAM PF2P.FOR
C    Procedure to extract parameters F0, T, and Epsilon
C    Set of data containing frequencies [kHz],
C    real (XD), and imaginary (YD) components of the dielectric
C    spectrum.

C    Prior to inputting them into this program, XD and YD should be
C    scaled by one or other of two methods ;
C    Alternative 1 : Picofarads
C         X : Parallel capacitance
C         Y : Parallel conductance/omega

C    Alternative 2 : Nondimensional
C         X : Epsilon prime
C         Y : Epsilon double prime
C    Where :
C    OMEGA : 2*PI*FD(I),IN KILO RADIANS/SEC

C    Values for both scaling alternatives are directly taken
C    from output of DIEL.

     CHARACTER*30 DESCR
     CHARACTER*12 DATIN
     COMMON /A/NDAT,II,FD(30),XD(30),YD(30),SND,R3,R4,IPA(4),MM
     COMMON /C/E0,E02,EI,E1,T1,B1,C1,E2,T2,B2,C2,F0,SR,F1,F2
     COMMON /Z/IS,IE

     C    READ IN DATA INTO FD, XD, AND YD ARRAYS

     WRITE(5,*)' Please input number of file sets to be fitted
     1 and fitting step '
     READ(5,*)NSET,MM
     K=0
10   WRITE(5,*)' Please input file name '
     WRITE(3,20)
20   FORMAT('1')
     READ(5,30)DATIN
30   FORMAT(A)

     WRITE(5,*) ' PLEASE INPUT THE STARTING POINT AND ENDING POINT TO
     1 CALCULATE RESIDUALS FOR SECANT '
     READ(5,*)IS,IE

     WRITE(5,*)' Please input order four numbers corresponding to '
     WRITE(5,*)' four frequencies you have selecsted for point-fit'
     READ(5,*)N1,N2,N3,N4
      IPA(1) = N1 ;  IPA(2) = N2
      IPA(3) = N3 ;  IPA(4) = N4

     OPEN(UNIT=1,DEVICE='DSK',FILE=DATIN)
```

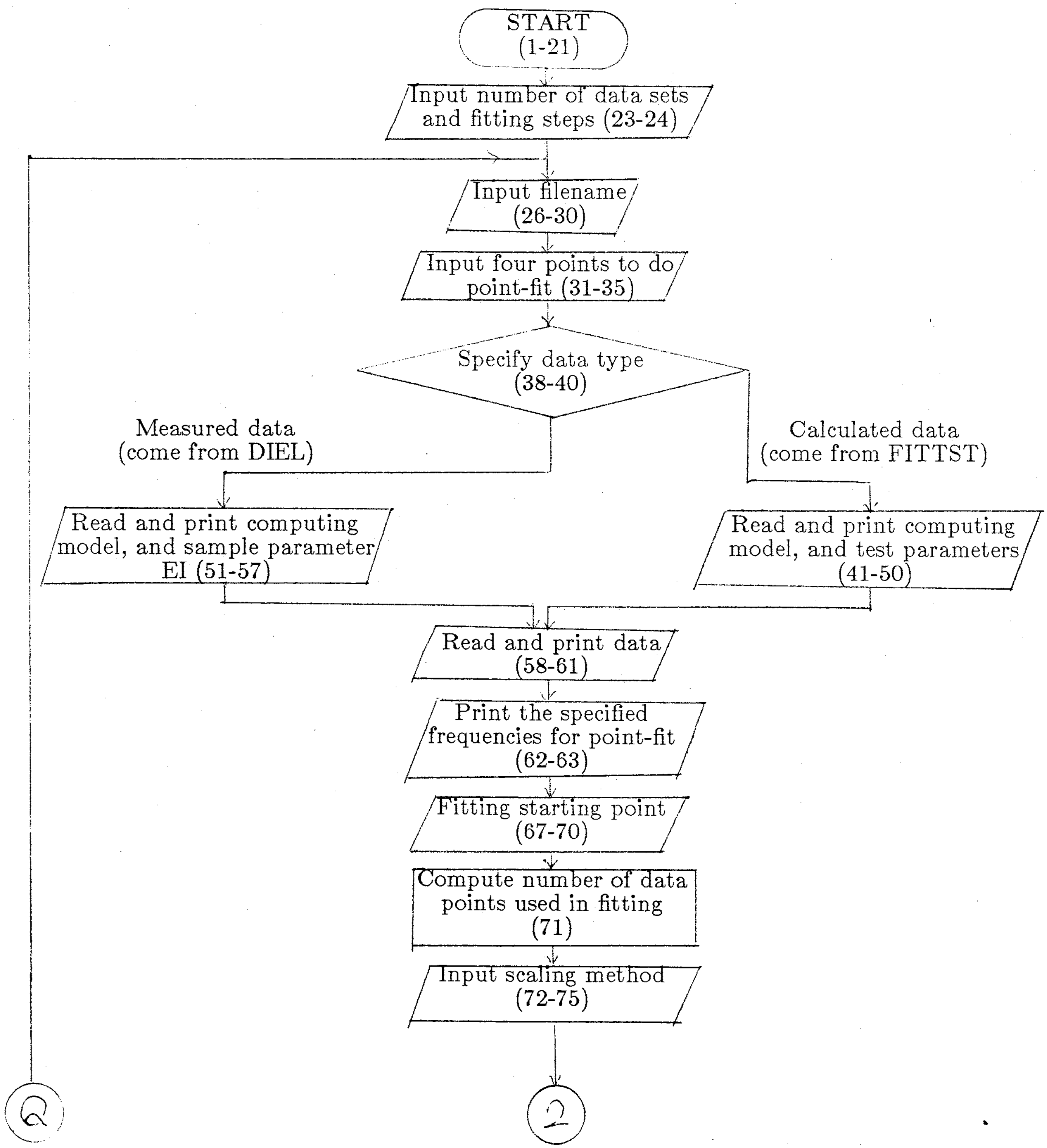
```
C       SPECIFY THE DATA TYPE

        WRITE(5,*)' Are these modelling data ? type YES for "model data" '
        WRITE(5,*)' & type NO for "measured data" '
        READ(5,30)TEST
        IF(TEST.EQ.'YES')THEN
        READ(1,30)DESCR
        READ(1,40)TE0,TE1,TE2,TT1,TT2,TF0,TEI
  40    FORMAT(1X,7F)
        WRITE(3,*)'     PF2P MODEL     '
        WRITE(3,50)DESCR
  50    FORMAT(A/)
        WRITE(3,*)' THESE TEST DATA ARE GENERATED FROM FOLLOWING
        1      PARAMETERS : '
        WRITE(3,60)TE0,TF0,TEI,TE1,TE2,TT1,TT2
  60    FORMAT(/,7X,'E0 = ',F12.4,4X,'F0 = ',F12.4,4X,'EI = ',
        1       F12.4,/7X,'E1 = ',F12.4,4X,'E2 = ',F12.4
        1       ,/7X,'T1 = ',F12.4,4X,'T2 = ',E12.4/)
        EI=TEI
        ELSE
        READ(25,30)DESCR
        WRITE(3,*)'     PF2P MODEL     '
        WRITE(3,50)DESCR
        WRITE(5,*)' PLEASE INPUT "EI" '
        READ(5,*)EI
        ENDIF

        READ(1,70)NDAT
  70    FORMAT(I)
        READ(1,80) (FD(I),XD(I),YD(I), I=1,NDAT)
  80    FORMAT(3F)

        CLOSE(UNIT=1)

        TPI=6.2831853
        TPIK=TPI*1000.

        WRITE(3,85)FD(N1),FD(N2),FD(N3),FD(N4)
  85    FORMAT(1X,' FIT P FOR RELAXATION COEFFICIENTS USING', 4(F8.5,2X)
        1 ,'kHz')

        WRITE(3,86)IS,IE
  86    FORMAT(/2X,' E0 WAS DETERMINED BY SECANT METHOD USING POINT ',I2,
        1 '-',I2/)
        WRITE(5,*)' PLEASE INPUT STARTING POINT '
        READ(5,*)II
        WRITE(3,90)II
  90    FORMAT(/2X,'FITTING STARTING POINT = ',I3/)
        SND=(NDAT-II)/MM+1

        WRITE(5,*)' Please input method for scaling the data
        1 "A1" or "A2" '
        READ(5,30)SWITCH
        WRITE(3,95)SWITCH
```

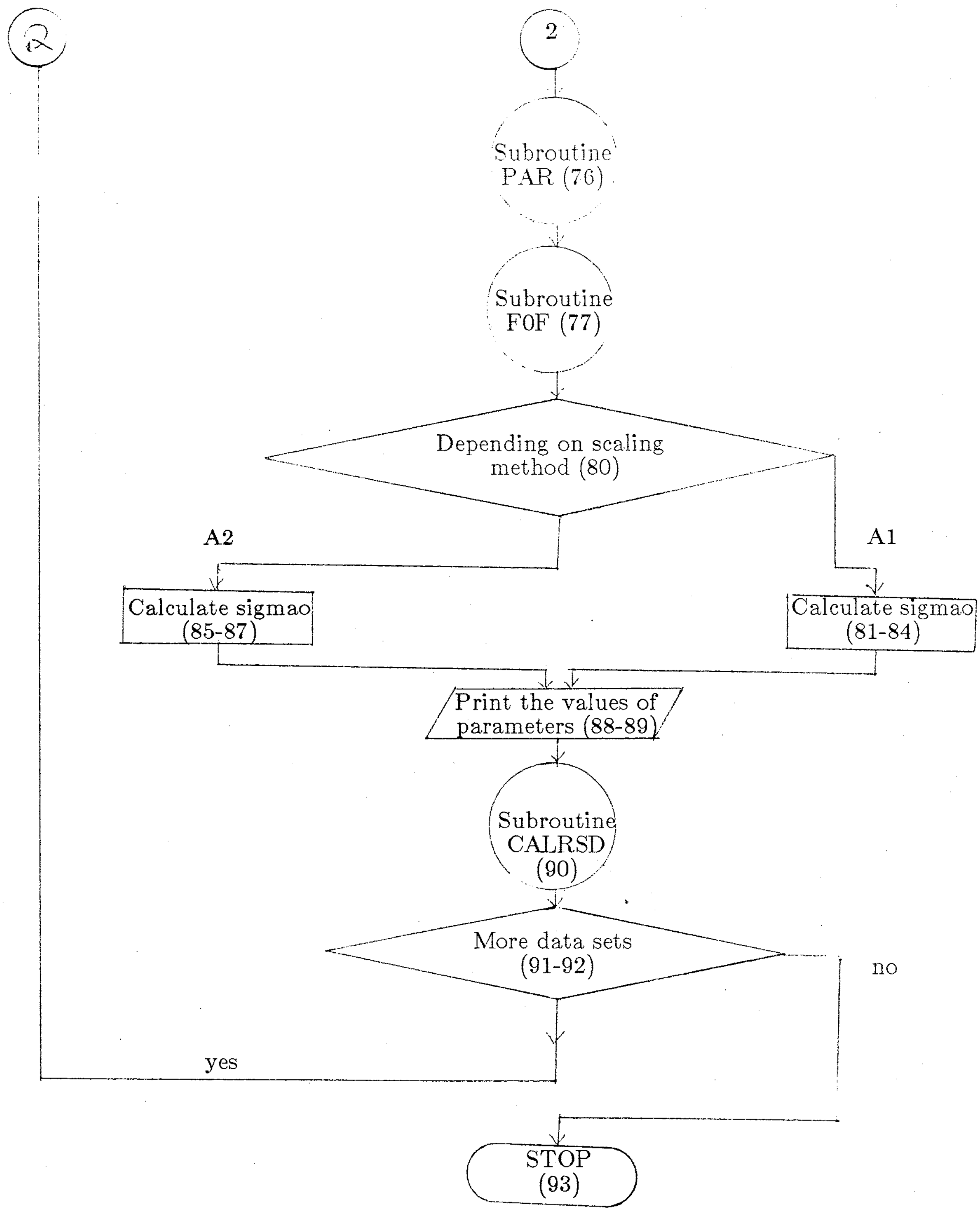
```
95    FORMAT(2X,'Scaling : Alternative ', 2A)

      SF2 = 0. ;  SF4 = 0.0
      DO 100 I = II, NDAT, MM
      FF = FD(I)**2 ; SF2 = SF2 + FF
100   SF4 = SF4 + FF**2

      CALL SEC

      CALL F0F

      TAU1=T1/TPIK
      TAU2=T2/TPIK

      IF (SWITCH .EQ. 'A1' ) THEN
      WRITE(5,*) ' A1 method need input geometrical factor "A/L" '
      WRITE(5,*) ' for calculating the Sigma0 '
      READ(5,*) AL
      SIGMA0=TPIK*F0*1.0E-12/AL
      ELSE
      SIGMA0=TPIK*F0*8.85E-14
      ENDIF
      WRITE(3,110) E0,F0,TAU1,E1,E2,TAU2,T1,T2,SIGMA0,B1,B2,EI,C1
      1 ,C2,F1,F2
110   FORMAT(/,7X,'E0 = ',F12.6,4X,'F0 = ',F12.4
      1,4X,'TAU1=',E12.4/7X,'E1 = ',F12.4,4X,'E2 = ',F12.4
      1,4X,'TAU2=',E12.4/7X,'T1 = ',F12.4,4X,'T2 = ',F12.4
      1,4X,'SIGMA0=',E12.4/7X,'B1 = ',F12.4,4X,'B2 = ',F12.4
      1,4X,'EI=',F12.4,/7X,'C1 = ',F12.4,4X,'C2 = ',F12.4/,7X,
      1'F1 = ',F12.4,4X,'F2 = ',F12.4)

      CALL CALRSD

      K = K + 1
      IF(K .GE. NSET) STOP
      GO TO 10
      STOP
      END


C     SEC subroutine
C     Uses a secant method to extrapolate E0

      SUBROUTINE SEC
      COMMON /A/NDAT,II,FD(30),XD(30),YD(30),SND,R3,R4,IPA(4),MM
      COMMON /C/E0,E02,EI,E1,T1,B1,C1,E2,T2,B2,C2,F0,SR,F1,F2
      COMMON /Z/IS,IE

      WRITE(3,5)
      k=0
      ff1=fd(1)**2   ;  ff2=fd(2)**2  ; r=ff2/ff1
      x1=xd(1)       ;  x2=xd(2)
      et=x1*(1.+(x1-x2)/(r*x2-x1))
```

```
      E0=ET ; CALL PAR ; RR=SR
      D=X1-E0
      WRITE(3,2)K,E0,SR,D,E1,E2,C1,C2

      K=1
      A12=FF1            ;        A13=X1*A12
      A22=FF2            ;        A23=X2*A22
      A32=FD(3)**2       ;    X3=XD(3)        ;    A33=X3*A32
      A31=1./A33         ;    A32=A32/A33     ;    X3=X3/A33
      A11=1.-A13*A31     ;    A12=A12-A13*A32 ;    X1=X1-A13*X3
      A21=1.-A23*A31     ;    A22=A22-A23*A32 ;    X2=X2-A23*X3

      E0=(A22*X1-A12*X2)/(A11*A22-A12*A21)

      WRITE(3,2)K,E0,SR,D,E1,E2,C1,C2
      D=ET-E0

      DO 4 K=2,15
      CALL PAR
      D=D*SR/(RR-SR)
      WRITE(3,2)K,E0,SR,D,E1,E2,C1,C2
      E0=E0-D
      IF(ABS(D).LT.(.0005))GO TO 8
4     RR=SR
8     K=K+1
      CALL PAR
      WRITE(3,2)K,E0,SR,D
5     FORMAT(/2X,'K',10X,'E0',14X,'SR',14X,'D',15X,'E1',14X,'E2',
     1 14X,'C1',14X,'C2'/)
2     FORMAT(1x,I2,f16.6,6(F16.4))
      RETURN
      END
```

E5. PF2PQ flow sheet and listing

The flow diagram for PF2PQ




2
2
Subroutine
PAR (76)
Subroutine
F0F (77)
Depending on scaling
method (80)
A2
A1
Calculate sigmao
(85-87)
Calculate sigmao
(81-84)
Print the values of
parameters (88-89)
Subroutine
CALRSD
(90)
More data sets
(91-92)
no
yes
STOP
(93)

PF2PQ program listing

```
C     Program PF2PQ.FOR
C     Procedure to extract parameters F0, T, and Epsilon

C     Set of data containing frequencies [kHz],
C     real (XD), and imaginary (YD) components of the dielectric
C     spectrum.

C     Prior to inputting them into this program, XD and YD should be
C     scaled by one or other of two methods ;
C     Alternative 1 : Picofarads
C             X : Parallel capacitance
C             Y : Parallel conductance/omega
C     Alternative 2 : Nondimensional
C         X : Epsilon prime
C             Y : Epsilon double prime
C     Where :
C     OMEGA : 2*PI*FD(I),IN KILO RADIANS/SEC

C     Values for both scaling alternatives are directly taken
C     from output of DIEL.

      CHARACTER*30 DESCR
      CHARACTER*12 DATIN
      COMMON /A/NDAT,II,FD(30),XD(30),YD(30),SND,R3,R4,IPA(4),MM
      COMMON /C/EI,E1,T1,B1,C1,E2,T2,B2,C2,F0,SR,F1,F2

C     READ IN DATA INTO FD, XD, AND YD ARRAYS

      WRITE(5,*)' Please input number of data sets to be fitted
     1 and fitting step'
      READ(5,*)NSET, MM
      K = 0
10    WRITE(5,*)' PLEASE INPUT THE FILE NAME '
      WRITE(3, 20)
20    FORMAT('1')
      READ(5,30)DATIN
30    FORMAT(A)
      WRITE(5,*)' PLEASE INPUT ORDER NUMBERS CORRESPONDING TO'
      WRITE(5,*)' FOUR FREQUENCIES YOU HAVE SELECTED FOR POINT FIT'
      READ(5,*)N1, N2, N3, N4
      IPA(1)= N1  ; IPA(2)= N2
      IPA(3)= N3  ; IPA(4)= N4

      OPEN(UNIT=1,DEVICE='DSK',FILE=DATIN)

C     CHECK THE DATA TYPE

      WRITE(5,*)' Are these model data ? Type YES for "yes"
     1 and type NO for "no" '
      READ(5,30)TEST
      IF(TEST.EQ.'YES')THEN
```

```
      READ(1,30)DESCR
      READ(1,40)TE1,TE2,TT1,TT2,TF0,TEI
 40   FORMAT(6F)
      WRITE(3,*)'    PF2PQ Model '
      WRITE(3,50)DESCR
 50   FORMAT(A/)
      WRITE(3,*)' THESE TEST DATA ARE GENERATED FROM FOLLOWING
      1     PARAMETERS : '
      WRITE(3,60)TF0,TEI,TE1,TE2,TT1,TT2
 60   FORMAT(/7X,'F0 = ',F12.4,4X,'EI = ',F12.4
      1,/7X,'E1 = ',F12.4,4X,'E2 = ',F12.4
      1,/7X,'T1 = ',F12.4,4X,'T2 = ',E12.4/)
      EI=TEI
      ELSE
      READ(1,30)DESCR
      WRITE(3,*)'    PF2PQ Model '
      WRITE(3,50)DESCR
      WRITE(5,*)' Please input "EI" '
      READ(5,*)EI
      ENDIF

      READ(1,70) NDAT
 70   FORMAT(I)
      READ(1,80)(FD(I),XD(I),YD(I), I=1,NDAT)
 80   FORMAT(3F)
      WRITE(3,85)FD(N1),FD(N2),FD(N3),FD(N4)
 85   FORMAT(1X,'FIT P FOR RELAXATION COEFFICIENTS USING ',4(F8.5,2X)
      1  ,' kHz')

      CLOSE(UNIT=1)

      TPI=6.2831853
      TPIK=TPI*1000.0

      WRITE(5,*) ' PLEASE INPUT FITTING POINT'
      READ(5,*) II
      WRITE(3,90) II
 90   FORMAT(1X,/,'FITTING STARTING POINT = ' I3)
      SND=(NDAT-II)/MM + 1

      WRITE(5,*)' PLEASE INPUT METHOD FOR SCALING THE DATA,
      1 "A1" OR "A2" '
      READ(5,30)SWITCH
      WRITE(3,95)SWITCH
 95   FORMAT(2X,'Scaling : Alternative ', 2A)

      CALL PAR

      CALL F0F

      TAU1=T1/TPIK
      TAU2=T2/TPIK

      IF (SWITCH .EQ. 'A1') THEN
```

```
      WRITE(5,*)' A1 method need input geometrical factor "A/L" '
      WRITE(5,*)' for calculating SIGMA0 '
      READ(5,*) AL
      SIGMA0=TPIK*1.0E-12*F0/AL
      ELSE
      SIGMA0=TPIK*F0*8.85E-14
      ENDIF
      WRITE(3,110) F0,TAU1,E1,E2,TAU2,T1,T2,SIGMA0,B1,B2,C1,C2
110   FORMAT(/,7X,'F0 = ',F12.4
      1,4X,'TAU1=',E12.4/7X,'E1 = ',F12.4,4X,'E2 = ',F12.4
      1,4X,'TAU2=',E12.4/7X,'T1 = ',F12.4,4X,'T2 = ',F12.4
      1,4X,'SIGMA0=',E12.4/7X,'B1 = ',F12.4,4X,'B2 = ',F12.4
      1,4X,'EI=',F12.4,/7X,'C1 = ',F12.4,4X,'C2 = ',F12.4)

      CALL CALRSD

      K = K + 1
      IF (K .LT. NSET) GO TO 10
      STOP
      END


C     PAR subroutine
C     Computes dispersion parameters E1, E2, T1, T2
C     By point-fit between measured and computed
C     X, Y values at a number of measurement frequencies.

      SUBROUTINE PAR
      COMMON /A/NDAT,II,FD(30),XD(30),YD(30),SND,R3,R4,IPA(4),MM
      COMMON /C/EI,E1,T1,B1,C1,E2,T2,B2,C2,F0,SR,F1,F2
      I = IPA(1);      F = FD(I);  FF = F**2
      R1 = XD(I) - EI;  A12 = FF;   A13 = - R1*FF;  A14 = A13*FF

      I = IPA(2);      F = FD(I);  FF = F**2
      R2 = XD(I) - EI;  A22 = FF;   A23 = - R2*FF;  A24 = A23*FF

      I = IPA(3);      F = FD(I);  FF = F**2
      R3 = XD(I) - EI;  A32 = FF;   A33 = - R3*FF;  A34 = A33*FF

      I = IPA(4);      F = FD(I);  FF = F**2
      R4 = XD(I) - EI;  A42 = FF;   A43 = - R4*FF;  A44 = A43*FF

      A22 = A22 - A12; A23 = A23 - A13; A24 = A24 - A14; R2 = R2 - R1
      A32 = A32 - A12; A33 = A33 - A13; A34 = A34 - A14; R3 = R3 - R1
      A42 = A42 - A12; A43 = A43 - A13; A44 = A44 - A14; R4 = R4 - R1

      A23 = A23/A22;       A24 = A24/A22;       R2 = R2/A22
      A33 = A33 - A32*A23;  A34 = A34 - A32*A24;  R3 = R3 - A32*R2
      A43 = A43 - A42*A23;  A44 = A44 - A42*A24;  R4 = R4 - A42*R2

      A34 = A34/A33;       R3 = R3/A33
      A44 = A44 - A43*A34;  R4 = (R4 - A43*R3)/A44

      R3 = R3 - A34*R4;     R2 = R2 - A23*R3 - A24*R4
```

```
      R1 = R1 - A12*R2 - A13*R3 - A14*R4

      RT = .5*R3
      D = RT**2 - R4
      IF(D.GT.0.) GO TO 210
      WRITE(3,200)
 200  FORMAT('0NEGATIVE DISCRIMINANT')
      E1=RT  ; C1=R3  ;  E2=0.0   ;  C2=0.0
      GO TO 220

 210  C1 = RT + SQRT(D);              C2 = R4/C1
      E2 = (R2 - C2*R1)/(C1 - C2);    E1 = R1 - E2
 220  T1 = SQRT(ABS(C1));             T2 = SQRT(ABS(C2))
      B1 = E1*T1;                  B2 = E2*T2
      F1 = 1.0/T1;                 F2 = 1.0/T2

      WRITE(3,240)
 240  FORMAT(/2X,'K',6X,'E0',10X,'E1',10X,'E2',11X,'C1',10X,'C2'
      1 ,10X,'SR',10X,'D',/)
      WRITE(3,250)K,E0,E1,E2,C1,C2,SR,D
      FORMAT(1X,I2,F12.6,5(F12.4),E12.4)
      RETURN
      END

C     F0F subroutine
C     Computes the dc conductance parameter from the
C     measurement-derived q-values and computed values E, T at each
C     frequency, then averages them for display as one value.

      SUBROUTINE F0F
      COMMON /A/NDAT,II,FD(30),XD(30),YD(30),SND,R3,R4,IPA(4),MM
      COMMON /C/EI,E1,T1,B1,C1,E2,T2,B2,C2,F0,SR,F1,F2
      S = 0.
      DO 4 I = II,NDAT,MM

      F = FD(I);       FF = F**2
 4    S = S + YD(I)*FD(I)
      &        - (B1/(1. + C1*FF) + B2/(1. + C2*FF))*FF

      F0 = S/SND
      RETURN
      END


C     CALRSD subroutine
C     Computes residuals between fitted and measured values,
C     respectively of X, Y, P, Q, and FQ, rms deviations of
C     XY and PQ.

      SUBROUTINE CALRSD
      COMMON /A/NDAT,II,FD(30),XD(30),YD(30),SND,R3,R4,IPA(4),MM
      COMMON /C/EI,E1,T1,B1,C1,E2,T2,B2,C2,F0,SR,F1,F2
      DIMENSION PPP(30),QQQ(30),PDAT(30),QDAT(30)
```

```
      SUMXY = 0.0
      SUMPQ = 0.0
      SUMFQ = 0.0

      WRITE(3,400)
  400 FORMAT(//,T21,'MEASURED',T39,'CALCULATED',T60,'RESIDUALS',T79,
     1 '% DIFFERENCE',T97,'RMSXY',/T21,'--------',T39,'----------'
     1 ,T60,'---------',T79,'------------',T97,'-----',/1X,
     1 'FREQ. (K HZ)',T19,'X',T28,'Y',T38,'X',T48,'Y',T58,'X',T68,
     1 'Y',T78,'X',T88,'Y')
      DO 430 J = 1,NDAT
      FF = FD(J)**2
      P = EI + E2 / (1.0+ C2 * FF) + E1 / (1.0 + C1 * FF)
      SQ = F0 + ( B2/(1.0 + C2 * FF) + B1/(1.0 + C1 * FF))* FF
      Q = SQ / FD(J)
      PPP(J) = P
      QQQ(J) = Q
      XXX = P
      YYY = Q
      RESX = XXX - XD(J)
      RESY = YYY - YD(J)
      DIFX = RESX/XXX*100.0
      DIFY = RESY/YYY*100.0
      XRMS = SQRT(( RESX**2 + RESY**2) / (XXX**2 + YYY**2))*100.0
      PDAT(J) = XD(J)
      QDAT(J) = YD(J)
      IF(J.LT.II) GO TO 410

      SUMXY = SUMXY + ABS(XRMS)
  410 WRITE(3,420)FD(J),XD(J),YD(J),XXX,YYY,RESX,RESY,DIFX,DIFY,XRMS
  420 FORMAT(1X,F10.5,2F10.2,7F10.3)
  430 CONTINUE
      XYAVE = SUMXY / SND
      WRITE(3,440)XYAVE
  440 FORMAT(/T92,F10.3//)

      WRITE(3,450)
  450 FORMAT('1',/,1X,'PAGE : 2 ',//,T21,'MEASURED',T39,'CALCULATED',
     1 T60,'RESIDUALS',T79,'% DIFFERENCE',T97,'RMSPQ',/T21,'--------',
     1 T39,'----------',T60,'---------',T79,'------------',T97,'-----',
     1 /1X,'FREQ. (K HZ)',T19,'P',T28,'Q',T38,'P',T49,'Q',T58,'P',T68,
     1 'Q',T78,'P',T88,'Q')
      DO 470 J = 1,NDAT
      RESP = PPP(J) - PDAT(J)
      RESQ = QQQ(J) - QDAT(J)
      DIFP = RESP/PPP(J)*100.0
      DIFQ = RESQ/QQQ(J)*100.0
      PRMS = SQRT(( RESP**2 + RESQ**2)/( PDAT(J)**2 + QDAT(J)**2))*100.0
      IF(J.LT.II) GO TO 460

      SUMPQ = SUMPQ + ABS(PRMS)
  460 WRITE(3,420)FD(J),PDAT(J),QDAT(J),PPP(J),QQQ(J),RESP,RESQ,DIFP
     1 ,DIFQ,PRMS
  470 CONTINUE
```

```
      PQAVE = SUMPQ / SND
      WRITE(3,440)PQAVE

      WRITE(3,480)
480   FORMAT(//,T21,'MEASURED',T39,'CALCULATED',T60,'RESIDUALS',T79,
     1 '% DIFFERENCE',T97,'F0',/T21,'--------',T39,'----------'
     1 ,T60,'---------',T79,'------------',T97,'--',/1X,
     1 'FREQ. (K HZ)',T23,'FQ',T43,'FQ',T63,'FQ',T83,'FQ')

      DO 510 J = 1,NDAT
      FF = FD(J)**2
      FQDAT = FD(J) * QDAT(J)
      DIF = FQDAT - ( B1/(1. + C1 * FF ) + B2/(1. + C2 * FF)) * FF
      FQ = FD(J) * QQQ(J)
      RESFQ = FQ - FQDAT
      FQRMS = RESFQ / FQDAT*100.0

      IF(J.LT.II) GO TO 490
      SUMFQ = SUMFQ + ABS(FQRMS)
490   WRITE(3,500)FD(J),FQDAT,FQ,RESFQ,FQRMS,DIF
500   FORMAT(1X,F10.3,5X,F10.3,10X,F10.3,10X,F10.3,10X,F10.3,5X,F10.3)
510   CONTINUE
      FQAVE = SUMFQ / SND
      WRITE(3,520)FQAVE
520   FORMAT(/T77,F10.3//)
      RETURN
      END
```